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1. *Properties of the Oxides of Nitrogen. Part II. The Binary System* N_2O_3–H_2O.

By T. M. Lowry and J. T. Lemon.

The object of the work now described was to determine the limits of miscibility of nitrous anhydride and water, with a view to complete a triangular phase diagram for the ternary system H_2O–N_2O_3–N_2O_5. Since the quantitative preparation of mixtures of nitrous anhydride and water was difficult and troublesome, the opportunity was also taken to plot an equilibrium diagram showing the freezing points as well as the limits of miscibility of a series of mixtures in the system N_2O_3–H_2O.

The earliest indication of the formation of two liquid layers in this system is afforded by the work of Luck (*Z. anal. Chem.*, 1869, **8**, 402), who purified nitrous anhydride, greenish-blue owing to contamination by the peroxide, by adding a little ice-cold water to the strongly cooled liquid.* The latter thereupon became pure indigo-blue, and, after separation of the upper aqueous layer, was rectified at 5—10°, the receiver being cooled in ice and salt. A similar observation of the effect of adding a small proportion of water to nitrous anhydride was also made by Mallet and Gaines (*Chem. News*, 1883, **48**, 97).

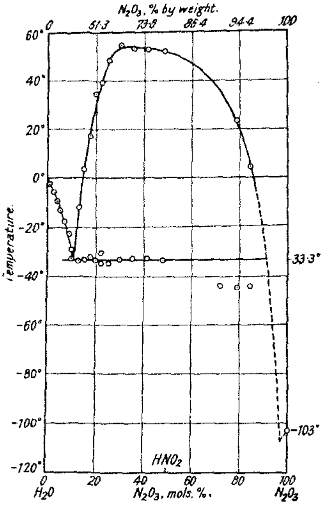
H. B. and M. Baker stated in 1907 (J., **91**, 1866) that liquid " nitrogen trioxide . . . is very little, if at all, soluble in water." This statement again suggests the formation of two liquid layers; but the first clear evidence that these can exist as stable liquid phases in equilibrium with one another was provided by Briner and Durand (*Compt. rend.*, 1912, **155**, 583, 1495), who stated that, " on adding a small quantity of water to N_2O_3, which, in the liquid state, is a very dark blue, one observes the appearance of a second upper blue liquid phase; then, on continuing the additions of water, the blue coloration pales, until it is no longer appreciable." They also recorded that " During the dilution, the pressure increases, then diminishes after passing through a maximum "; but no numerical or experimental details are given in this note.

The existence of two liquid layers in mixtures of nitrous anhydride and water was confirmed by preliminary experiments made in this laboratory by Dr. W. V. Lloyd; but the high gaseous pressures blew out the stop-cocks of the apparatus, so the two layers were observed only in mixtures from which a little nitric oxide had escaped. Improved methods of working have now made it possible to avoid this loss of nitric oxide, so the total composition of the mixtures used in the present series of observations was accurately known. It was not practicable, however, to prevent a redistribution of nitric oxide between the liquid and the gaseous phase. Hence, since the latter always contains an excess of nitric oxide, the liquids must be slightly richer in oxygen and the aqueous layer may therefore contain a little nitric acid. This unavoidable change of composition was reduced to a minimum by making sure that the volume of liquid was at least equal to 40% of the total

* Fritzsche (*J. pr. Chem.*, 1841, **22**, 14) had attempted to prepare nitrous anhydride by adding ice-water to chilled nitrogen peroxide, but was unable to separate the two layers on account of the violent boiling which occurred on pouring; he was therefore obliged to distil them both together, after allowing them to become warm, and collected the anhydride in the first fraction.

volume; moreover, most of the essential observations were made under conditions in which the pressure of nitric oxide was not excessive. The results of the experiments are set out in the table and plotted in Fig. 1.

Fig. 1.



Equilibrium diagram for nitrous anhydride and water.

The limits of composition within which two liquid layers are formed are approximately 48—95% N_2O_3 by weight at 20° and 42—97% at 0°. These limits are believed to be correct within about 1%, but at higher temperatures the expulsion of nitric oxide from the liquid phases into the gaseous phase becomes a serious source of error. We therefore record, with full recognition of their tentative character, the observations which showed that the liquids in the tubes became completely miscible at temperatures above 55°, and that this maximum in the miscibility curve was reached at a composition of 65% N_2O_3 by weight or 30 mols. %. The general form of the curve suggests that the critical solution temperature may be perhaps 20° higher than the figure recorded above, and that the critical composition may be much nearer to that of nitrous acid than these figures would indicate.

Below 0° the solubility of nitrous anhydride in water falls to 36% by weight at − 33·3°. At this temperature the solubility curve intersects the freezing-point curve for homogeneous solutions of the anhydride in water. Four phases are in

Freezing Points and Temperatures of Separation into Two Layers in Mixtures of Nitrous Anhydride and Water.

Composition, by wt.			H_2O content.		Vol. occupied by liquid, %.	F. p.	Turb. pt.
H_2O, g.	N_2O_4, g.	NO, g.	Wt., %.	Mols., %.			
1·9092	0·0560	0·0365	95·39	98·86	54·0	− 2·1°	
1·8064	0·1174	0·0766	90·31	97·50	49·3	− 5·6	
1·7870	0·1893	0·1235	85·10	96·00	53·3	− 8·5	
1·7660	0·2665	0·1738	80·04	94·40	53·3	− 13·0	
1·6532	0·3308	0·2157	75·16	92·73	49·5	− 17·8	
1·5658	0·4041	0·2635	70·12	90·83	42·3	− 22·6	
1·5039	0·4804	0·3133	65·45	88·88	45·0	− 29·0* − 32·7	} < − 40°
1·5007	0·5796	0·3780	61·04	86·87	48·3	− 33·8	− 12·0
1·3069	0·6141	0·4005	56·30	84·47	42·9	− 33·1	+ 3·5
1·2183	0·6819	0·4446	51·96	82·07	43·8	− 32·2	+ 17·3
0·9380	0·6029	0·3931	48·50	79·90	45·1	− 33·3	+ 34·5
1·1178	0·8272	0·5394	44·99	77·53	53·1	− 30·6	+ 39·0
0·6885	0·5142	0·3354	44·76	77·38		− 34·3	
1·0034	0·8773	0·5720	40·90	74·49	44·8	− 34·8	+ 48·2
0·9117	1·0104	0·6589	35·32	69·73	52·8	− 33·4	+ 54·9
0·7800	1·1099	0·7239	29·84	64·22	52·3	− 32·6	+ 53·6
0·6511	1·1854	0·7732	24·96	58·38	50·0	− 32·8	+ 53·3
0·5435	1·3019	0·8488	20·17	51·60	53·0	− 33·7	+ 52·3
0·1558	1·0432	0·6802	8·30	27·60	42·7	− 44·2	
0·1060	1·0383	0·6769	5·82	20·69	43·3	− 45·4	+ 23·5
0·0796	1·1563	0·7540	4·00	14·95	45·0	− 44·2	+ 4·6

* − 29·0° refers to a point on the ice line, and − 32·7° to one on the eutectic line.

equilibrium at this quaternary point, *viz.*, (i) a vapour phase, consisting mainly of nitric oxide, (ii) an aqueous phase, consisting mainly of aqueous nitrous acid with free nitrous anhydride, $2HNO_2 \rightleftharpoons H_2O + N_2O_3$, (iii) a heavy blue liquefied gas phase, containing more than 94% N_2O_3, and (iv) a colourless solid phase of pure ice.

The temperature of separation of ice should remain constant at $-33{\cdot}3°$ so long as two liquid layers are present; but in practice, lower freezing points were recorded in mixtures containing more than 50 mols. % N_2O_3. This may perhaps be attributed to the escape into the gaseous phase of an appreciable amount of nitric oxide from mixtures richer in N_2O_3 than nitrous acid itself.

It would be expected that, when the aqueous layer had dissolved completely in an excess of nitrous anhydride, the freezing point would fall to another quaternary point below the freezing point of nitrous anhydride at $-103°$ (Wittorff, *Z. anorg. Chem.*, 1904, **41**, 85), but no attempt was made to extend the observations to this range of concentrations.

Colour of the Mixtures.—When the tubes containing the mixtures were removed from the bath of liquid nitrogen used in preparing them, the contents remained almost colourless * for about 3 minutes, after which the strong blue colour of nitrous anhydride appeared suddenly. It is probable that this compound begins to be formed at $-112°$, the eutectic temperature of nitrogen peroxide and nitrous anhydride (*idem, ibid.*), at which a liquid phase first becomes possible in the system. The vapour pressure of nitric oxide at this temperature is about 28 atm., according to Olszewski (*Compt. rend.*, 1885, **100**, 940); but Adwentowski (*Bull. Acad. Cracow*, 1909, 742) gives the pressure as 21·6 atm. at $-112{\cdot}6°$.

Dilute solutions of nitrous anhydride in water are colourless, but the blue colour of the anhydride begins to be apparent, in columns of 10 cm., at a concentration of about 5% N_2O_3, or at about 10% N_2O_3 when viewed in the narrow sealed tubes. The colour is still weak at 15 and 20% N_2O_3, but becomes fairly strong at 25 and 30%. At higher concentrations, the solutions in the sealed tubes begin to look like a blue ink; but the aqueous phase is still transparent to transmitted light even at concentrations at which two liquid layers are formed.

The aqueous layers are pure blue at room temperatures. Those mixtures which were heated to 35—40° during the observations of turbidity developed a marked greenish tint, and those which were heated above 45° became deep green; but the original pure blue colour was invariably restored on cooling to room temperature.

The lower layer, which separates from mixtures containing more than about 48% by weight of nitrous anhydride, consists mainly of this oxide. It is mobile, like liquid nitrogen peroxide, and is considerably denser than the aqueous layer. At room temperatures it is such a deep blue as to be transparent only in thin layers. It has a slight greenish tinge which becomes more marked when the temperature is raised.

EXPERIMENTAL.

Materials.—(i) *Nitric oxide.* This was prepared by dropping aqueous sodium nitrite into a concentrated solution of ferrous sulphate containing about one-tenth of its volume of sulphuric acid (Thiele, *Annalen*, 1889, **253**, 246), and was collected in an aspirator over water. The apparatus used for purifying it, and for preparing mixtures of nitrous anhydride and water, is shown in Fig. 2; it was originally constructed by Dr. W. V. Lloyd and used by him for preparing mixtures of the former with nitrogen peroxide.

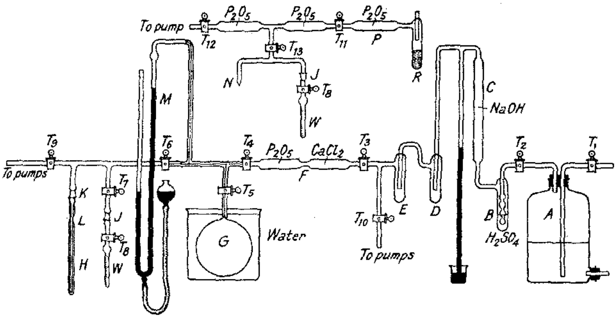
Purification was effected substantially as described by Purcell and Cheesman (J., 1932, 826). For this purpose the whole apparatus was first evacuated to a pressure of less than 0·01 mm. by means of a mercury-diffusion pump backed by an oil pump, and all the taps were closed. Nitric oxide was then admitted slowly from the aspirator *A*, through the sulphuric acid bubbler, *B*, and a column *C* packed with pieces of caustic soda. It was condensed and frozen to a solid in the trap *D* by means of liquid nitrogen. A little nitrogen, present as an impurity in the nitric oxide, remained uncondensed; it was pumped away, and washed out by allowing a little of the nitric oxide to evaporate. The nitric oxide was then sublimed into a second trap *E*, and the purific-

* The solid or liquid nitric oxide showed a weak blue colour. A light reddish (burnt Sienna) colour was sometimes seen in patches where gaseous nitric oxide was in contact with solid N_2O_4; but in presence of blue N_2O_3 this appeared as a light purple tint.

ation repeated. The tap T_4 was then closed and T_5 opened. The nitric oxide in E was allowed to liquefy and evaporate, and was passed through the drying tubes, F, into the bulb G; the last fraction was retained in E and was finally excluded by closing the tap T_4.

The bulb G and manometer M constituted a gas-measuring apparatus from which known quantities of nitric oxide could be drawn (cf. Baume and Robert, *Compt. rend.*, 1909, **148**, 1322; 1919, **169**, 968; Maass and Russell, *J. Amer. Chem. Soc.*, 1918, **40**, 1847). For this purpose the bulb was immersed in a thermostat, and the level of the mercury in the manometer M was always brought to the 90-cm. mark on the scale before reading the pressure. The volume of the bulb G (907·2 c.c.) and of the connecting tubes T_4, T_5, T_6, M to the 90-cm. mark (20·3 c.c.) had been determined previously by alternately exhausting them and then filling them (three times) with dry air from a gas burette. Since the capacity of the capillary connecting tubes was only a little more than 2% of that of the bulb, and their temperature did not often differ from that of the bath by more than 3°, the error introduced by deviations of the room temperature from that of the bath could be neglected.

FIG. 2.



(ii) *Nitrogen peroxide.* Purified liquid nitrogen peroxide was supplied in sealed Carius tubes by the Research Department of Messrs. Nobel's Explosives Company, Ardeer, and was handled by methods already developed by Dr. Ellis Lloyd. For this purpose, the Carius tube was first cooled in ice and cracked open. The open end was connected by a glass tube, firmly sealed on with paraffin wax, to a receiver R (Fig. 2, inset) of about 100 c.c. capacity, provided with a phosphoric oxide tube P. The nitrogen peroxide was then distilled over from the Carius tube by immersing the receiver in liquid air and reducing the pressure with a water-pump. When the receiver was full, the connexion leading to the Carius tube was sealed off at a constriction. The receiver with its drying tube was then exhausted to less than 1 mm. with an oil-pump and sealed off in a vacuum.

When required, the receiver was attached to the filling apparatus (Fig. 2, inset), but the nitrogen peroxide was kept frozen as long as possible, and transferred from one vessel to another by sublimation under low pressure, in view of the fact that the Apiezon L grease, which was used as a lubricant for taps and ground joints in these investigations, was noticeably attacked if exposed to this gas at ordinary pressures for more than short periods (about 10—15 minutes).

The nitrogen peroxide was weighed in a graduated tube W (Fig. 2), provided with a tap T_8 and ground-glass joint J. For this purpose the tube W was evacuated and weighed, and was then attached to the filling apparatus by means of the ground joint J. The nitrogen peroxide in the receiver R was frozen in liquid air, and the apparatus was exhausted to less than 1 mm. The tap T_{13} was then closed, and a suitable quantity of nitrogen peroxide sublimed into W by cooling it in liquid air, whilst the receiver R was allowed to warm up somewhat. Taps T_8 and T_{13} were then closed. The weighing tube W was removed, the ground joint J cleaned with light petroleum, and the tube rapidly weighed to give the exact weight of nitrogen peroxide taken. The peroxide was immediately frozen in liquid air, and the tube attached to the nitric oxide apparatus shown in Fig. 2.

Preparation of Mixtures.—The mixtures were prepared in tubes of soda glass, of 4·5—5 mm. bore and with walls 1·5—2 mm. thick; these had a final over-all length of 23 cm. and a capacity of about 4 c.c. The tube *H* was constricted at *L* with special care in view of the pressures which it had to withstand. A suitable quantity of water was first introduced and frozen by immersing the tube in liquid nitrogen. The tube was then attached to the measuring and filling apparatus by means of the ground-glass joint *K*, and the nitrogen peroxide, which had been weighed in the graduated tube *W*, was distilled over into it. Finally, gaseous nitric oxide from the measuring bulb *G* was condensed in quantities corresponding with the equation $NO + NO_2 = N_2O_3$. The tubes in which the three layers had been frozen were sealed off as robustly as possible, and allowed to warm to room temperature in a box covered with a sheet of plate glass. This precaution was fully justified by the bursting of 4 out of 27 tubes during the dangerous stage between the vaporisation of the nitric oxide and its absorption by the other components of the mixture.

Measurement of Temperature.—Temperatures below 0° were obtained by immersing the tubes in alcohol (about 1500 c.c.) in a transparent Dewar flask, and cooling the alcohol by blowing liquid nitrogen on the surface (Rupert, *J. Amer. Chem. Soc.*, 1909, **31**, 851; Terrey and Spong, J., 1932, 219), or by the addition of solid carbon dioxide. The alcohol was stirred mechanically, and a copper–constantan thermocouple was used to measure its temperature. This couple had been calibrated at the m. p.'s of ice, purified carbon tetrachloride (– 22·9°), and mercury (–38·87°). Before observations were made, the tubes were cooled and shaken, in order to absorb as much nitric oxide as possible. They were illuminated from behind, and viewed under magnification by a lens system.

Temperatures above 0° were obtained by using a clear glass vessel containing water, with the same arrangements for stirring and observation. The temperature of the water was controlled by adding hot or cold water or ice as required. Observations above room temperature were made through a cage of wire gauze as a protection in case the tube should burst when warmed.

(i) The separation of ice was always accompanied by supercooling; this was overcome by dipping the tip of the tube into acetone cooled with solid carbon dioxide, and then replacing the tube in the bath. The bath was allowed to warm spontaneously at a rate of 5—10° per hour, and the temperature was recorded (at least three times) at which the last residue of ice began to melt.

(ii) Points on the eutectic line represent the temperature at which melting began in the frozen aqueous layer, as indicated by the movement of globules of the blue "liquefied gas" phase entangled in the crystals of ice.

(iii) The formation of two liquid layers was observed by cooling mixtures which had been rendered homogeneous by warming and shaking. Turbidity appeared suddenly in the aqueous solution, and the temperatures of separation could be reproduced within 0·3°. At the lower temperatures the progressive absorption of nitric oxide from the gas phase on repeated cooling and shaking caused a rise in the temperature at which turbidity appeared: this was as much as 2° at + 3° and 8° at – 10°. The temperatures of separation recorded in the table must therefore be regarded only as minimum values; but they vary so rapidly with changes of concentration that no substantial error is likely to be introduced in our estimate of the critical composition for complete miscibility at atmospheric temperatures, or below.

(iv) Further evidence of the rapid change of the temperature of separation with variations of composition in the lower part of the curve was provided by the behaviour of a super-cooled mixture (No. 7) containing 34·45% N_2O_3. This should have deposited ice at a temperature a little above the quaternary point at – 33·3°, at which a mixture containing 36% N_2O_3 deposits ice and becomes turbid simultaneously. Actually, it was super-cooled to – 40° without becoming turbid; and even when ice was beginning to appear at temperatures below – 40°, no turbidity was developed during the crystallisation.

(v) At concentrations greater than 52% N_2O_3, the temperatures of separation rise more slowly, since the curve is already bending over towards a maximum. Moreover, the increased proportion of nitrous anhydride in the aqueous layer makes the solutions so dark that the separation into two layers is difficult to observe. The highest temperature of separation was 55°, at which complete miscibility occurred in a composition of 65% N_2O_3 or 30 mols. %.

(vi) The mixtures richest in nitrous anhydride developed the highest pressures whilst being allowed to warm to room temperature. The proportion of free space in the tube was therefore increased to rather more than one-half, and the solid nitrogen peroxide was distributed over the walls of the tube in order to increase the area of contact during the absorption of the nitric oxide. The limits of composition within which two liquid layers are formed on this side of the solubility

curve are very narrow, but two mixtures containing 94·2 and 96·0% N_2O_3 gave observed temperatures of separation of 23·5° and 4·6°.

(vii) The limits of miscibility read off from the curve are 48·6 and 94·5% by weight N_2O_3 at 20°, 42·4 and 96·3% at 0°. Since these limits are brought closer together by the passage of nitric oxide into the gaseous phase, a small correction was introduced automatically by selecting integral percentages *below* and *above* the observed decimal readings on the *left* and the *right* arm of the curve respectively. We therefore estimate the limits of partial miscibility in integral percentages as 48—95% N_2O_3 at 20°, 42—97% N_2O_3 at 0°, and regard it as unlikely that these are in error by more than one unit.

SUMMARY.

1. Two liquid phases are formed over a wide range of composition in mixtures of nitrous anhydride and water.

2. The limits of miscibility (by weight) are 42—97% N_2O_3 at 0° and 48—95% at 20°. A maximum temperature of separation was observed at 55° in a mixture containing 65% N_2O_3 or 30 mols. %; but these figures are all lowered by the escape of nitric oxide from the liquid phases into the gaseous phase, and in particular, the critical solution temperature may be as much as 20° higher than the limit thus recorded.

3. A quaternary point, at which one gaseous and two liquid phases are in equilibrium with pure ice, was observed at − 33·3° and 36% N_2O_3. A second quaternary point, with nitrous anhydride as the solid phase, may be expected to occur below − 103° at a concentration greater than 98% N_2O_3.

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2. *Properties of the Oxides of Nitrogen. Part III. The Pseudo-binary System* N_2O_4–H_2O.

By T. M. LOWRY and J. T. LEMON.

UNLIKE the binary system N_2O_3–H_2O (Part II, preceding paper), where internal oxidation and reduction are only of secondary importance, the components of the pseudo-binary system N_2O_4–H_2O do not merely dissolve in one another, or unite to form a hydrate, but interact reversibly to give products of a higher and a lower degree of oxidation, as shown by the equation

$$H_2O + 2N_2O_4 \rightleftharpoons N_2O_3 + 2HNO_3 \quad . \; . \; . \; . \; . \; . \; . \quad (i)$$

When the initial proportion of N_2O_4 exceeds about 50%, two liquid layers are formed, *viz.*, (i) a liquefied gas layer consisting almost entirely of N_2O_3 and N_2O_4, and (ii) an aqueous acid layer, containing nitric acid, a smaller proportion of nitrous acid, and a considerable amount of dissolved N_2O_3 and N_2O_4. A second form of interaction, represented by the equation

$$3N_2O_4 + 2H_2O = 4HNO_3 + 2NO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (ii)$$

(Schönbein, *J. pr. Chem.*, 1860, **81**, 268), may result in the escape of nitric oxide into the gaseous phase, and thus produce a change in the composition of the liquid; but the pressures of nitric oxide developed in this way are smaller than in the system N_2O_3–H_2O; the interaction represented by equation (i) is therefore here much more important than that by equation (ii). These equilibria are of considerable industrial interest in connexion with the manufacture of nitric acid, and have therefore been studied extensively from this point of view; * but the phase-rule study here described appears to be entirely novel.

* Saposchnikoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 506; Förster and Koch, *Z. angew. Chem.*, 1908, **21**, 2161, 2209; Lewis and Edgar, *J. Amer. Chem. Soc.*, 1911, **33**, 292; Partington and Parker, *J. Soc. Chem. Ind.*, 1919, **38**, 75; Förster, Burchardt, and Fricke, *Z. angew. Chem.*, 1920, **33**, 113, 122, 129; Rideal, *J. Ind. Eng. Chem.*, 1920, **12**, 536; Sanfourche, *Ann. Chim. Phys.*, 1924, **1**, 5; Klemenc *et al.*, *Z. anorg. Chem.*, 1924, **141**, 231, *et seq.*; Abel *et al.*, *Z. physikal. Chem.*, 1928, **132**, 55, *et seq.*; Abel, Schmid, and Stein, *Z. Elektrochem.*, 1930, **36**, 692; see also Webb, "The Absorption of Nitrous Gases" (Arnold).

The earliest observations on the interaction of nitrogen peroxide and water were made by Priestley (" Experiments and Observations on Different Kinds of Air," Vol. 3, p. 198), who passed the gas through three wash-bottles in series containing water, and observed that the water, after becoming warm, began to " sparkle " and evolve gas; it then became successively blue, green, and finally yellowish-green. The gas which escaped from the last wash-bottle was found to be nitric oxide. He also placed some of the green solution in an open dish and blew upon it, whereupon copious red vapours were evolved, leaving a yellow residue of nitric acid (*op. cit.*, p. 204).

Dulong (*Ann. Chim. Phys.*, 1816, **2**, 317) found that a very small quantity of water was sufficient to turn liquid nitrogen peroxide green; when poured drop by drop into water, the liquid fell to the bottom and became a very deep green. He also observed that, on adding successive amounts of liquid nitrogen peroxide to water, the evolution of nitric oxide diminished and finally ceased, although the liquid still continued to take up the peroxide. During the addition, the water exhibited the same changes of colour as were observed on passing nitric oxide through aqueous nitric acid of various concentrations.

Fritzsche and Mitscherlich in 1832 observed that, when liquid nitrogen peroxide was allowed to take up water slowly from the air, two green liquids were formed, which separated again after shaking, like those given by nitrogen peroxide and nitric acid. Fritzsche (*J. pr. Chem.*, 1841, **22**, 14) separated and distilled the two liquid layers produced by the gradual addition of water to liquid nitrogen peroxide cooled in ice and salt. The lower, dark green layer began to boil at 17°, giving an almost pure blue distillate; the temperature then rose gradually to 28°, whilst the liquid lost its green colour and finally showed the yellow-brown colour of nitrogen peroxide. The upper, grass-green layer began to boil at 20°, and a few drops of blue liquid collected in the cooled receiver; the boiling point then rose rapidly to 120°, at which the pale yellow residue of aqueous nitric acid distilled unchanged. When a larger quantity of water was added to liquid nitrogen peroxide, the lower blue-green layer was so dark as to be transparent only in thin layers. On distilling this mixture, without separating the two layers, the lower layer began to boil below 0°, liberating nitric oxide, and giving a pure indigo-blue distillate of nitrous anhydride; when redistilled, this began to boil again below 0°, with evolution of nitric oxide, giving an indigo-blue distillate in the cooled receiver; but the boiling point gradually rose to 28°, the residue consisting of nitrogen peroxide. From his experiments, Fritzsche concluded that nitrous anhydride decomposes into nitric oxide and nitrogen peroxide on distillation, and that the green colour of the liquid products was due to the admixture of deep blue nitrous anhydride with yellow-brown nitrogen peroxide.

Similar conclusions regarding the origin of the green colours in mixtures of nitrogen peroxide and water were reached by Briner and Durand (*Compt. rend.*, 1912, **155**, 583, 1495), who found that these mixtures behaved in much the same way as mixtures of nitrous anhydride and water (see Part II). Finally, Heberlein (Thesis, Geneva, 1926), by measurements of conductivities, confirmed the totally different character of the two liquid layers, since the lower layer of liquefied gas had a specific resistance of the order of 10^6 ohms, whereas that of the upper aqueous acid layer was of the order of 2—12 ohms.

Experimental.

The methods used in the present investigation were as described in Part II, but the preparation of the mixtures was simplified by the omission of nitric oxide from the components. The results are set out in the table and plotted in the figure. Three of the mixtures had been prepared by Dr. W. V. Lloyd; the observations now made with these specimens are shown by crossed circles in the figure. The limits of miscibility at 0° and 20°, which he deduced from his analyses, are indicated by crosses, as follows:

At 0°: 49·9 and 98·2% by wt. (or 16·3 and 91·4 mols. %) N_2O_4
At 20°: 53·0 and 97·2% by wt. (or 18·1 and 87·2 mols. %) N_2O_4

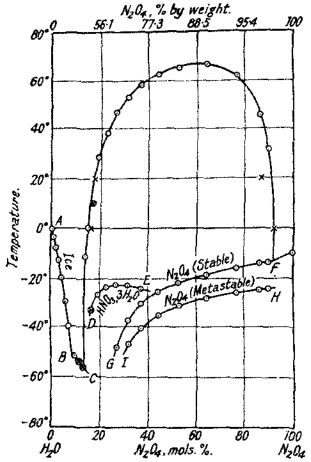
With the exception of the higher limit at 20°, which appears to be in error, these numbers conform closely with the measurements now recorded.

Description of the Equilibrium Diagram.—(*a*) The curve *AB* represents the temperature of

crystallisation of ice from the homogeneous aqueous solutions. Beautiful fern-like growths were frequently obtained when freezing was initiated by cooling the tip of the tube with solid carbon dioxide; but at the lower temperatures the increasing viscosity of the aqueous solutions caused the crystals to grow more slowly, and compact clumps of ice were produced. The temperatures were recorded at which the first signs of melting were observed.

(*b*) At about $-50{\cdot}3°$ and 32·7% N_2O_4, the ice-line is intersected by a short curve *BC*, corresponding to the crystallisation of some new compound. This compound (which was not observed in the system N_2O_3–H_2O) crystallised in cubic aggregates, which were obviously different from ice: it is perhaps a hydrate of nitric or nitrous acid, but its composition was not determined.

(*c*) The curve *DE* represents the temperature of separation, from the aqueous acid layer, of a compound which crystallised in long prisms with triangular facets at the ends. This was almost certainly the trihydrate of nitric acid, which was described by Pickering (J., 1893, **63**, 436) as forming "rather transparent large crystals." This identification is justified by the fact that the maximum of the curve at $-22{\cdot}5°$ lies only 4° below that of the trihydrate in the system HNO_3–H_2O, where it has a considerable range of existence (Küster and Kremann, *Z. anorg. Chem.*, 1904, **41**, 22); moreover, in each case the freezing-point curve has a flat maximum, indicating that it is largely dissociated on fusion. On the other hand, the monohydrate, even in pure aqueous solutions, has a maximum freezing point at $-38°$, which could not be *raised* to $-22°$ by the presence of other components in our mixtures.



Equilibrium diagram for nitrogen peroxide and water.

(*d*) At higher concentrations of nitrogen peroxide, the upper aqueous layer deposited yellow crystals when cooled with acetone and solid carbon dioxide, but the temperatures of separation were not determined. When the tubes were then placed in a bath at $-30°$, the yellow crystals soon developed a green and then a blue colour and decomposed with much bubbling, leaving a residue which appeared to consist of solid nitrogen peroxide. These crystals were probably the compound, $N_2O_4,2HNO_3$, which Pascal and Garnier (*Bull. Soc. chim.*, 1919, **25**, 309) described as decomposing at $-48{\cdot}5°$.

(*e*) The two roughly parallel curves *FG* and *HI* represent the temperatures of crystallisation of nitrogen peroxide from the lower layer of *liquefied gas*. This layer consists almost entirely of nitrogen peroxide and nitrous anhydride and its f. p. falls continuously, from right to left of the diagram, as the concentration of the nitrous anhydride increases (by the elimination of the higher oxide as nitric acid) when the proportion of water is increased. The f. p. of the layer was recorded as the temperature at which the first signs of melting could be observed in a small quantity of solid in contact with the solution.

The upper curve *FG* corresponds to separation of the ordinary stable form of nitrogen peroxide, in small bright granular crystals, or occasionally in aggregates of hexagonal crystals. The lower curve *HI* represents the crystallisation of a new, metastable form of the peroxide. This was obtained as the initial product by chilling the tube in a bath of alcohol cooled by carbon dioxide, and then holding the tip of the tube in contact with solid carbon dioxide to initiate crystallisation; but it reverted to the stable form when the contact was continued, or the tube was sharply tapped. The new form usually crystallised in long, broad needles, like sword blades, which soon acquired irregular and serrated edges as growth continued; but pointed and diamond-shaped crystals were occasionally observed, the latter sometimes fused together to form sheets with serrated edges. In addition, the solid often separated as an ice-like crust on the walls of the tube; but all

Freezing Points and Temperatures of Separation into Two Layers in Mixtures of Nitrogen Peroxide and Water.

Composition by wt.		H_2O content.		Vol. occupied by liquid,	Freezing points.				Solid phase separating from aq. layer.
						Liquefied gas.			
N_2O_4, g.	H_2O, g.	Wt., %.	Mols., %.	%.	Aqueous layer.	N_2O_4, ordinary form.	N_2O_4, new form.	Turb. pt.	
0·1241	2·6333	95·50	99·10	76·8	− 3·3°	—	—	—	Ice
0·2743	2·5607	90·30	97·94	77·8	− 7·5	—	—	—	,,
0·4117	2·3810	85·27	96·73	68·3	− 12·5	—	—	—	,,
0·5494	2·2601	80·43	95·46	73·2	− 19·5	—	—	—	,,
0·7233	2·1705	75·00	93·88	70·4	− 29·3	—	—	—	,,
0·8593	2·0432	70·38	92·40	66·1	− 39·9	—	—	—	,,
1·0307	1·9379	65·29	90·58	69·4	− 51·2	—	—	—	New solid
L_1		61·20	88·96	71·8	− 53·0	—	—	—	,,
L_2		56·62	86·95	48·5	− 55·4	—	—	—	,,
0·7540	0·9207	54·97	86·18	67·0	*	—	—	− 10·9° †	
0·7837	0·8865	53·08	85·25	62·6	*	—	—	− 0·1 †	
L_3		49·40	83·30	52·4	− 32·7	—	—	+ 10·5 †	$HNO_3,3H_2O$
1·7936	1·4419	44·56	80·38	68·2	− 26·4	—	—	28·9 †	,,
2·1169	1·3766	39·40	76·85	72·5	− 23·7	—	—	38·7 †	,,
2·3449	1·2295	34·40	72·82	73·2	− 22·5	− 47·4°	—	47·1 †	,,
2·5976	1·0756	29·28	67·90	69·2	− 22·8	− 37·0	− 46·6°	53·3 †	,,
2·7846	0·9042	24·52	62·39	73·3	− 23·9	− 30·2	− 40·0	58·5 ‡	,,
1·6363	0·3997	19·63	55·49	73·3	—	− 25·4	− 35·0	62·4 ‡	
1·8309	0·3198	14·86	47·14	77·1	—	− 22·1	− 31·1	65·5 ‡	
1·8705	0·2007	9·70	35·43	74·7	—	− 18·8	− 28·2	66·8 †	
2·0629	0·1201	5·50	22·92	81·8	—	− 16·0	− 26·1	61·9 †	
2·0128	0·0617	2·98	13·55	74·4	—	− 14·2	− 24·8	45·7 †	
2·0154	0·0437	2·12	9·96	75·2	—	− 13·6	− 24·2	31·8 †	

L_1, L_2, L_3 = mixtures prepared by W. V. Lloyd.

* In these two mixtures the aqueous phase remained very turbid after cooling, and its freezing point could not therefore be determined.

† Globules fall. ‡ Globules rise.

Since the eutectic of the N_2O_3–N_2O_4 system is situated at about − 112° (cf. Baume and Robert, *Compt. rend.*, 1919, **169**, 968; Wittorff, *Z. anorg. Chem.*, 1904, **41**, 90), it might be expected that the temperatures of separation of the peroxide from these more complex mixtures would fall to a still lower temperature. The extension of the curves *FG*, *HI* to lower temperatures could not be observed, however, for the lower layer became so intensely blue that it was extremely difficult to observe melting, even when the tube was inverted so that the lower layer filled the pointed end; moreover, this difficulty was accentuated by the fact that the lower layer tended to remain a little turbid. An approximate idea of the composition of the lower layer at its f. p. can be derived from the f. p.'s of the system N_2O_4–N_2O_3, as plotted by the above authors, since the ready and complete volatility of this layer shows that it contains only minimal amounts of water or nitric acid in addition to the two main components.

(*f*) The miscibility curve, *CF*, is similar in general shape to the corresponding curve for the system N_2O_3–H_2O, but is rather flatter and more symmetrical when plotted on a scale of mols. %. The limits of miscibility deduced from this curve are

At 0° : 46·9 and 98·4% by wt. (14·7 and 91·5 mols. %) N_2O_4
At 20° : 52·3 and 98·1% by wt. (17·7 and 90·8 mols. %) N_2O_4

The highest observed temperature of separation was at 67° in a mixture containing 89% N_2O_4 (62 mols. %), but the real critical solution temperature must be a little higher, and at a rather lower concentration of N_2O_4, on account of the escape of nitric oxide from the liquid phases into the gaseous phase. The displacement is, however, obviously much smaller than in the system N_2O_3–H_2O, because the pressures developed were much less, so that none of the tubes burst either on warming or on subsequent heating, although some of them were heated above 70°. Moreover, the volume of the gaseous phase was reduced from about 60% of the total volume in the system N_2O_3–H_2O to about 25% in the system N_2O_4–H_2O, so the errors introduced from this cause would be relatively small.

SUMMARY.

1. Two liquid phases are formed over a wide range of compositions in mixtures of nitrogen peroxide and water.

2. The limits of miscibility (by weight) are 47—98% N_2O_4 at 0° and 52—98% N_2O_4 at 20°. A maximum temperature of separation was observed at 67° in a mixture containing 89% N_2O_4 (62 mols. %); but these figures may be slightly lowered by the escape of nitric oxide from the liquid phases into the gaseous phase.

3. The homogeneous aqueous solutions deposit ice at temperatures down to − 50° and compositions up to 33% N_2O_4. They then deposit a compound of unknown composition over a narrow range down to − 56° and up to 44% N_2O_4. Non-homogeneous mixtures, containing more than 44% N_2O_4, deposit the trihydrate of nitric acid from the upper aqueous-acid layer, at temperatures which reach a maximum of − 22·5° at a gross composition of about 67% N_2O_4 for the whole mixture. The lower layer of liquefied gas deposits nitrogen peroxide, either in the ordinary stable form or in a metastable form which melts about 11° lower.

We are indebted to the Imperial Chemical Industries, Limited, for a maintenance grant to one of us (J. T. L.), during the period in which the research described in Parts II and III was carried out.

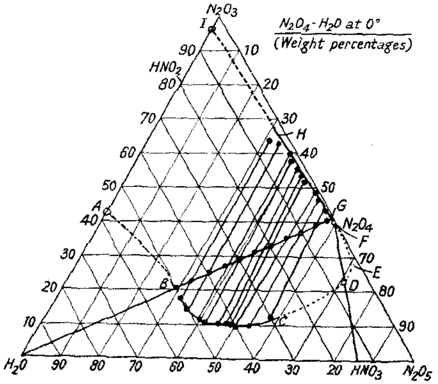
LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE UNIVERSITY. [*Received, October 9th*, 1935.]

3. *Properties of the Oxides of Nitrogen. Part IV. Formation of Two Liquid Layers in Mixtures of Nitrogen Peroxide and Water.*

By T. M. LOWRY, ELLIS LLOYD, and W. V. LLOYD.

IN the two preceding papers, the limits of miscibility of the aqueous and the non-aqueous layers, formed by mixtures of nitrous anhydride and of nitrogen peroxide with water, have been determined up to the temperature of complete miscibility. In the binary system

FIG. 1.



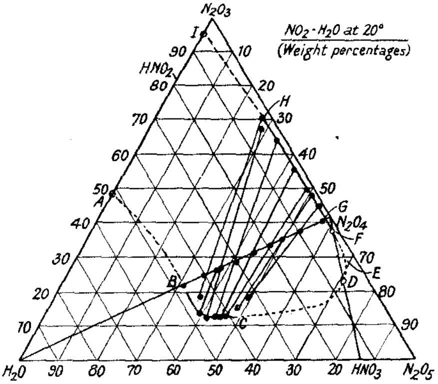
N_2O_3–H_2O, the compositions of these layers appear to be substantially constant at a given temperature (compare ether and water, or phenol and water); it was therefore possible to represent the freezing points of the aqueous layer over a considerable range of total compositions by a horizontal straight line. In the pseudo-binary system N_2O_4–H_2O, this was no longer possible, since the compositions of the two layers were influenced by mutual oxidation

and reduction to an extent which depended on the relative masses of the components. The freezing points of the two liquid layers were therefore represented by *curves* instead of by straight lines; but no attempt was made to determine the compositions of these layers under the conditions then prevailing.

The present paper describes experiments (carried out earlier), in which analyses of the two liquid layers, formed by mixtures of nitrogen peroxide and water, were made at two temperatures only, *viz.*, 0° and 20°. The data thus obtained are recorded as % by weight in Table I, and in mols. % (for 0°) in Table II. They have also been plotted on triangular diagrams (Figs. 1 and 2), the *apices* of which are formed by the three components of the system H_2O–N_2O_3–N_2O_5, whilst the compositions of N_2O_4, HNO_2, and HNO_3 are shown on the *sides* of the diagram.

Each mixture of nitrogen peroxide and water is represented by three points on the diagram, one showing the empirical composition of the mixture, and the other two showing

FIG. 2.



the actual compositions of the two layers. These three points are joined by a tie-line, and the ends of these tie-lines provide two substantial sections, *BC*, *GH*, of the boundary, *ABCDEFGHI*, of the area of the diagram within which two liquid phases are formed. Since complete separation of the two liquid layers was always difficult, the boundary line has been drawn through the outermost points on the tie-lines.

It was not practicable in the time available to plot the whole of this boundary, but the measurements in Part III provide independent data for the two points *BG* at which the boundary intersects the line H_2O–N_2O_4. Similarly, the observations recorded in Part II show that the miscibility curve cuts the H_2O–N_2O_3 side of the diagram at two widely separated points, *AI*, instead of forming a closed loop, as we supposed when we first began to plot the tie-lines. Quantitative experiments then showed that the aqueous boundary *BA* actually bends away from the non-aqueous boundary, *GHI*, in a manner that involves a reversal of curvature, when compared with the section *BC* of the boundary which had already been plotted. The data for the system N_2O_3–H_2O are, however, quite precise; and the broken lines, *AB* and *HI*, which link them with the results of the present analyses, are so nearly straight that no wide deviation from them appears to be likely to result from subsequent experimental determinations.

Two additional points, *DF*, on the other side of the H_2O–N_2O_4 line, are provided by Bousfield's measurements (J., **1919**, **115**, 45) of the limits of miscibility in the system

N_2O_4-HNO_3. These two points have been joined by a broken curve, which does not diverge very far from the N_2O_4-HNO_3 line. The line *DF* between them provides an additional tie-line on the diagram; but it is much shorter than those now recorded for mixtures of nitrogen peroxide and water, since the peroxide mixes more readily with nitric acid than with water. The broken curve indicates that complete miscibility would occur in mixtures of nitric acid and the peroxide with a little nitric anhydride. This additional component appears to mix in all proportions, both with the peroxide and with the acid, up to a limit fixed by the solubility of the solid; it would therefore distribute itself somewhat evenly between the aqueous and the non-aqueous layer, and finally reduce them to identity of composition. The tie line *DF* would then vanish at the point *E*.

One of Bousfield's points, *F*, on the line N_2O_4-HNO_3 is very close to our own point, *G*, on the N_2O_4-H_2O line, and forms only a slight extension of the boundary line, *HG*. The other point, *D*, is much more isolated; but we have ventured to join it by a continuous broken line *DC* to our own curve *BC* for the aqueous layer. It must be emphasised, however, that the broken curve, *CDEF*, passes through only one experimental point, and that (apart from the complete miscibility of water and nitric acid) we have no other check upon unexpected deviations from the course suggested.

The diagram emphasises the interesting contrast between nitric anhydride, which is completely miscible, and the peroxide and sesquioxide, which are only partially miscible, with water. These two lower oxides do not differ very widely in this respect. The zone in which two liquid layers are formed therefore forms a wide strip, the boundaries of which are nearly parallel to the side of the triangular diagram which includes the three oxides. Both boundaries are, however, concave when viewed from the opposite apex, and show some tendency to be pivoted on the point, H_2O, with a minimum of solubility in water at the composition N_2O_4. When, however, the non-aqueous components have been oxidised about half-way between N_2O_4 and N_2O_5, they become almost abruptly miscible with water in all proportions, since the boundary *CD* at 20° is not far removed from a straight line passing through the " water " point on the diagram.

Densities of Liquid Phases.—The densities of a series of homogeneous mixtures of nitrogen peroxide and water were determined by the method of flotation; but this became difficult to apply in mixtures containing more than 44% N_2O_4, and had to be abandoned altogether above 50% N_2O_4, where two liquid layers were formed; the intense colours of such solutions prevented proper observation of the floats, even under strong illumination, and the use of narrower observation tubes proved impracticable, because the floats tended to adhere to the wall of the vessel. In such solutions, and especially in systems containing two liquid layers, it was also found that the floats themselves adhered together very obstinately. In these circumstances the densities of the two liquid layers were determined by means of a capillary pyknometer. For this purpose mixtures were prepared in a separator of the type illustrated in Fig. 4, but with narrow pyknometer tubes in place of the bulbs D_1 and D_2. The ready formation of comparatively stable emulsions, however, made it impracticable to obtain data for mixtures containing 34—47% of water.

The numerical results are summarised in Table IV, and are plotted in Fig. 3.

In these mixtures the non-aqueous layer was always the denser and the more strongly coloured. This does not remain true, however, throughout the ternary system, since density measurements have substantiated the fact that, in mixtures of nitrogen peroxide with nitric acid, the *lower* layer consists of nitric acid with dissolved nitrogen peroxide, whilst the *upper* layer consists mainly of liquid nitrogen peroxide (Pascal and Garnier, *Bull. Soc. chim.*, 1919, **25**, 309; Bousfield, *loc. cit.*). Hence, in the ternary system, the densities of the two layers must become identical and change over at a contour line on the triangular equilibrium diagram lying between the lines representing the two binary systems HNO_3-N_2O_4 and H_2O-N_2O_4. This reversal of densities was actually observed in mixtures of nitrogen peroxide and water by Heberlein (Thesis, Geneva, 1926, p. 20), who states that, at 4% H_2O the aqueous layer " is always heavier than the layer of liquefied gas," that " at 6% H_2O, the two layers have nearly the same density," whilst " at 8% H_2O and above, the aqueous layer rises to the surface." Observations by Lowry and Lemon,

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

A meeting under the auspices of the Society and in conjunction with the University of Birmingham Chemical Society was held in the Chemistry Lecture Theatre of the University at Edgbaston on Monday, December 2nd, 1935, at 5 p.m., when Professor G. Barger, F.R.S., gave a lecture on "Alkaloids. General Ideas and Methods." At the conclusion of the lecture a vote of thanks to the Lecturer was carried with acclamation.

On Monday, December 9th, 1935, at 5 p.m., Dr. R. G. W. Norrish lectured on "The Decomposition of Molecules by Light" before an appreciative audience and a cordial vote of thanks was given to the Lecturer.

Ordinary Scientific Meeting, held in the Lecture Theatre of the Royal Institution (by the courtesy of the managers) on Thursday, January 16th, 1936, at 8 p.m. Professor N. V. SIDGWICK, C.B.E., M.A., D.Sc., F.R.S., President, was in the Chair.

The PRESIDENT referred to the loss sustained by the Society through the deaths of the following Fellows :—

	Elected.	Died.
John Harold Edge	1909	12th October, 1932.
John K. H. Inglis	1904	19th September, 1935.
William A. McCubbin	1890	10th January, 1936.
Thomas H. Pope	1898	12th January, 1936.
Francis Ransom	1889	19th December, 1935.

The PRESIDENT announced that

1. *The names of the members of Council who retire at the next Annual General Meeting,* and who are ineligible for the same office until after the lapse of one year, are as follows :—

Vice-Presidents who have filled the office of President : Professor G. G. HENDERSON and Professor W. P. WYNNE.

Vice-Presidents who have not filled the office of President : Professor F. G. DONNAN and Professor C. S. GIBSON.

Ordinary Members of Council—

(a) *Town Members :* Dr. J. KENYON, Dr. G. A. R. KON, and Mr. J. DAVIDSON PRATT.

(b) *Country Members :* Dr. R. G. W. NORRISH, Dr. E. H. RODD, and Professor R. WHYTLAW-GRAY.

In April 1935, Professor R. Robinson was appointed to fill the vacancy among Vice-Presidents who have not filled the office of President caused by the election of Professor N. V. Sidgwick to the office of President, and in June Professor H. E. Armstrong was appointed to fill the vacancy among Vice-Presidents who have filled the office of President caused by the death of Sir James Walker. The appointments were until the next Annual General Meeting; these two vacancies, therefore, fall due to be filled.

In December last, the Council accepted the resignation of Professor S. Sugden from the office of Honorary Secretary, as from the date of the next Annual General Meeting. This vacancy also falls due to be filled.

The following vacant places in the Council fall due to be filled at the Annual General Meeting of the Society, which will be held at the University, Bristol, on Thursday, April 16th, 1936, at 4.15 p.m. :—

Vice-Presidents who have filled the office of President .... *Three vacancies.*
Vice-Presidents who have not filled the office of President .... *Three vacancies.*
Honorary Secretary .... *One vacancy.*

Ordinary Members of Council—

(a) *Town Members* (*i.e.* those living within a radius of 50 miles from Charing Cross) .... *Three vacancies.*
(b) *Country Members* (*i.e.* those living beyond a radius of 50 miles from Charing Cross) .... *Three vacancies.*

In accordance with Bye-Law VI the Council has made the following nomination :—

Honorary Secretary : Professor J. W. Cook.

2. The Council had sent congratulations to the following Fellows who were included in the list of New Year Honours :—

Knights Bachelor.

Mr. Bryce Chudleigh Burt, C.I.E., M.B.E., B.Sc.
Professor Arthur Harden, D.Sc., F.R.S.

Order of the British Empire.

Professor Shanti Sarup Bhatnagar, D.Sc.

Forms of Recommendation for Fellowship were read for the first time in favour of :

John Desmond Bernal, M.A., 68, Walnut Tree Avenue, Cambridge.
Charles Edwin Clarkson, B.Sc., " Greylow," Chilcompton, Bath.
Antony Lester Elliott, 68, Rotton Park Road, Edgbaston, Birmingham, 16.
Sydney John Mortimer Fisher, B.A., B.Sc., Rydal School, Colwyn Bay.
Fred Hulse, 33, Grove Road, Halton, Leeds.
Harry Munroe Napier Hetherington Irving, M.A., B.Sc., D.Phil., A.I.C., L.R.A.M., 2B, Crick Road, Oxford.
Helen Mackay McKenzie, M.A., B.Sc., 12, Irvine Place, Aberdeen.
Ewart Marsden, B.Sc., 3, West View, Hipperholme, Halifax.
William McGillivray Morgan, B.Sc., 59, Church Road, Gosforth, Newcastle-on-Tyne, 3.
Leonard Alfred O'Neill, M.Sc., 20, Shirland Road, Maida Hill, W. 9.
John Alfred Rawlinson, 24, Rosemary Gardens, East Sheen, S.W. 14.
Basil Roland Record, B.Sc., 9, Woodville Road, Harborne, Birmingham.
John Chapman Smith, M.P.S., 18, Francis Road, Acocks Green, Birmingham.
Augustus William Wellings, M.Sc., 27, Acacia Road, Leamington Spa, Warwickshire.

and also of the following, whose applications have been accepted by the Council under Bye-Law I (2) :

Suryakant Rupshanker Oza, B.A., B.Sc., Shri Shakti Alkali Works, Dhrangadhra, India.
Albert S. Richardson, A.M., Ph.D., The Procter and Gamble Co., Ivorydale, Ohio, U.S.A.

Forms of Recommendation for Fellowship in favour of 14 Candidates were read for the second time.

A Discussion on " Stereochemistry " was opened by Dr. W. H. Mills. The following took part in the discussion :

Dr. P. Maitland on " Allene Dissymmetry."
Professor S. Sugden on " Stereochemistry of 4-Co-ordination Compounds of the Transitional Elements."
Professor Alexander McKenzie on " Stereochemistry of Intramolecular Changes."
Dr. E. E. Turner on " Stereoisomerism Dependent on Restricted Rotation about a Single Bond."

Dr. William Wardlaw, Mr. E. G. Cox, Dr. J. Kenyon, and Dr. A. Weissberger also joined in the discussion.

A vote of thanks to the Officers and Managers of the Royal Institution for the use of the Lecture Theatre, moved by the PRESIDENT, was carried with acclamation.

List of papers, or abstracts thereof, received between December 19th, 1935, and January 16th, 1936. (This List does not include the titles of papers which have been read at an *Ordinary Scientific Meeting, or which have appeared in the Journal.)*

"The apparent dipole moments of benzene, diphenyl, carbon disulphide, etc., when dissolved in polar solvents." By (Mrs.) C. G. LE FÈVRE and R. J. W. LE FÈVRE.

"Studies in chelation. Part III. The stabilisation of Kekulé forms in *o*-hydroxy carbonyl compounds." By W. BAKER and (MISS) O. M. LOTHIAN.

"Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. Part VIII. Energies associated with induced polar effects in the hydrolysis of substituted benzoic esters." By C. K. INGOLD and W. S. NATHAN.

"Mechanism of substitution at a saturated carbon atom. Part VI. Hydrolysis of *iso*propyl bromide." By E. D. HUGHES, C. K. INGOLD, and U. G. SHAPIRO.

"The mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. Part VII. Attack at a saturated carbon atom by a charged ion." By J. W. BAKER and W. S. NATHAN.

"Studies in the pyrone series. Part III. The influence of the phenyl group in the Kostanecki reaction." By I. M. HEILBRON, D. H. HEY, and B. LYTHGOE.

"15-Phenylpentadecoic acid and 22-phenylbehenic acid." By G. M. HILLS and R. ROBINSON.

"Tricosanoic and tetracosanoic acids and certain derivatives." By R. ASHTON, R. ROBINSON, and J. C. SMITH.

"Free radicals and atoms in primary photochemical processes. The free *n*-propyl radical." By T. G. PEARSON and R. H. PURCELL.

"Solvent effect in dipole moment measurements. The polarisation of chloro- and nitrobenzenes, chloroform, and bromoform in a series of polar solvents." By R. J. W. LE FÈVRE and P. RUSSELL.

"The apparent dipole moment of paraldehyde in various solvents." By R. J. W. LE FÈVRE and P. RUSSELL.

"Nitro- and amino-3-arylphthalaz-4-ones, and corresponding 1-methyl compounds." By F. M. ROWE, G. M. HEATH, and C. V. PATEL.

"Chlorination of toluene in presence of (*a*) activated charcoals, (*b*) iron-impregnated silica gel. Production of—side chain substitution—nuclear substitution—tolane derivatives." By J. B. FIRTH and T. A. SMITH.

"Some derivatives of 4 : 4′-diaminodiphenylmethane." By G. D. PARKES and R. H. H. MORLEY.

"Studies in graphite formation. Part II. The chemical nature of graphite and amorphous carbon." By A. E. BALFOUR, H. L. RILEY, and R. M. ROBINSON.

"Syntheses in the phenanthrene series. Part I. 2-Methoxy-1-methylphenanthrene." By P. HILL, W. F. SHORT, and (in part) (MISS) A. HIGGINBOTTOM.

"Studies on hydrogen cyanide. Part VII. Aldehydes from aromatic hydrocarbons." By L. E. HINKEL, E. E. AYLING, and J. H. BEYNON.

"Syntheses in the phenanthrene series. Part II. 7-Methoxy-1-methylphenanthrene and a new route to phenanthrene." By W. F. SHORT, H. STROMBERG, and A. E. WILES.

"Syntheses in the phenanthrene series. Part III. 9-Hydroxyphenanthrene." By I. R. SHERWOOD, W. F. SHORT, and J. WOODCOCK.

"Derivatives of chelidamic acid." By C. S. GIBSON and B. LEVIN.

"The organic compounds of gold. Part VI. Heterocyclic compounds containing gold." By A. BURAWOY and C. S. GIBSON.

"The action of nitrosyl chloride on *n*-hexane in presence of light." By S. MITCHELL and S. C. CARSON.
"*o*-Nitrophenylsulphenates of phenols." By E. K. LEARMONTH and S. SMILES.
"A rearrangement of carbamido-sulphones and sulphides." By W. J. EVANS and S. SMILES.
"The action of selenium dioxide on sterols and bile acids. Part II. *apo*Cholic acid and dihydroxycholenic acid. The formation of isomeric dihydroxycholadienic acids." By R. K. CALLOW.
"The action of ammonia upon esters." By F. D. CHATTAWAY.

FORMS OF RECOMMENDATION FOR FELLOWSHIP. THE BALLOT WILL BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, FEBRUARY 20th, 1936.

ABRAHART, EDWARD NOAH, 13, Silver Hill Rd., Derby. British. Research Student. B.Sc. (External), London University, 1934. Research, University College, Nottingham. *Date of birth Dec. 9th, 1911.* (*Signed by*) F. S. Kipping, E. B. R. Prideaux, H. H. Barber, B. D. Shaw, J. B. Firth.

AGAR, JOHN NEWTON, *24, Parsonage St., Cambridge. British. Research Student.* B.A., Cambridge. 1st class, Part II, Nat. Sci. Tripos (Chemistry), Cambridge, 1935. B.A. Research Scholarship, Sidney Sussex College. Date of birth Aug. 11th, 1914. (*Signed by*) Philip Bowden, T. M. Lowry, A. S. C. Lawrence.

BADDELEY, GEORGE, College of Technology, Manchester. British. Demonstrator. B.Sc., M.Sc., Ph.D. Sheffield University. Research Student at Sheffield University, 1930—1933. Demonstrator at the College of Technology, Manchester, since 1933. *J.C.S.*, 1933, 46, 261; 1934, 633; 1935, 303. (*Signed by*) J. Kenner, W. F. Short, W. Bradley.

BAKER, GEORGE PETER, 41, Preston Park Avenue, Brighton 6. British. Student at *Trinity College, Cambridge. Reading for Part II of the Natural Sciences Tripos* (*Chemistry*). Date of birth Aug. 14th, 1915. (*Signed by*) Peter Maitland, F. B. Kipping, F. G. Mann.

BASFORD, FREDERICK ROBERT, 101, Huntingtower Road, Grantham, Lincolnshire. British. B.Sc. (Hons. Chemistry), External, London University. Research Student, University College, Nottingham. Date of birth Dec. 16th, 1912. (*Signed by*) F. S. Kipping, E. B. R. Prideaux, H. H. Barber, B. D. Shaw, J. B. Firth.

BATEMAN, LESLIE CLIFFORD, 16, St. Stephens Rd., Yiewsley, Middlesex. British. Research Student. 1st Class Hons., London University. B.Sc. (Special) Chemistry, 1935 (degree will not be awarded until July 1936). Recently commenced research in Organic Chemistry at *University College, London. Date of birth March 21st, 1915.* (*Signed by*) E. D. Hughes, A. D. Scott, C. K. Ingold.

BENNETT, WILLIAM FRANK, 12, Chalk Pit Hill, Chatham, Kent. British. A.R.C.S., A.I.C. Analytical Chemist (War Department). (*Signed by*) A. I. Vogel, W. L. German, R. A. E. Galley.

BERNAL, JOHN DESMOND, 68, Walnut Tree Avenue, Cambridge. British. Assistant Director of Research in Crystallography. M.A., Cambridge. Many published papers on Structure of Crystals. Among them "The Structure of Graphite," *Proc. Roy. Soc.*, **1924**, **106**, 749. "The Metallic State," *Trans. Faraday Soc.*, 1929, 25, 367. "Calciferol," *Nature*, 1932, **129**, 277. "A Theory of Water and Ionic Solution," *J. Chem. Phys.*, **1933**, **1515**. "Pepsin," *Nature*, 1934, **133**, 794. "The Function of Hydrogen in Intermolecular Forces," *Proc. Roy. Soc.*, 1935, **151**, 384. "Structure of Some Hydrocarbons Related to the Sterols," *J.C.S.*, 1935, 93. "Annual Reports, Crystallography," 1928, 29, 30—31, 32—33. (*Signed by*) H. McCombie, F. G. Mann, R. G. W. Norrish.

BRANDT, CARL WILLIAM, c/o Dominion Laboratory, Sydney Street, Wellington, New Zealand. British. Assistant Analyst. M.Sc., University of New Zealand. Publications: "The Chemistry of Diterpene Compounds from the Woods of Dacrydium Species." Hosking and Brandt, *Ber. Deutsch. Chem. Ges.*, 1934, **67**, 1173; 1935, **68**, 37, 286, 1311. "The Alkaloid of *Senecio Jacobeus.*" Hosking and Brandt. *New Zealand Jour. of Science and Technology* (now in the printer's hands). (*Signed by*) J. S. Maclaurin, R. L. Andrew, W. Donovan.

BROOKMAN, ERNEST FRANCIS, 124, Durrington Rd., Clapton, E. 5. British. Research Assistant. B.Sc. (Special), University College, London. 1st Class Hons. in B.Sc. (Special),

Chemistry. Research Assistant to Dr. Norrish under D.S.I.R. at Cambridge. Date of birth July 6th, 1913. (*Signed by*) S. G. Foord, E. J. Buckler, R. G. W. Norrish.

BUSH, LEONARD ALBERT, 40, High Street, Kingswood, Bristol. British. Works Chemist. Holder of National Certificate in Chemistry. Engaged in Manufacturing Chemistry for 8 years. Student at Merchant Venturers' Tech. College. Date of birth April 9th, 1912. (*Signed by*) E. B. Maxted, M. Taylor, M. W. Travers, M. Nierenstein.

CLARKE, THOMAS ELLISS, 18, Oak Bank Avenue, Moston, Manchester 9. English. Student. B.Sc. (London—2nd Class Hons.), A.I.C., A.K.C. 3-Year Chemistry Course at King's College, London. At present am investigating the Variation of Apparent Molar Volume with Concentration. Date of birth Aug. 23rd, 1914. (*Signed by*) C. W. Davies, J. Kenyon, A. Houssa.

CLARKSON, CHARLES EDWIN, "Greylow," Chilcompton, Bath, Somerset. British. B.Sc., (Manchester). Senior Science Master, County Secondary School, Midsomer Norton, Bath. Been engaged in teaching of Chemistry for sixteen years. Joint paper with T. Malkin, "Alternation in Long-Chain Compounds. Part II. An X-Ray and Thermal Investigation of the Triglycerides." (*Signed by*) E. B. Maxted, M. Taylor, T. Malkin.

COWDREY, WILLIAM ARTHUR, 86*a*, Ingelow Rd., Battersea, S.W. 8. British. Research Student at University College. B.Sc. (Special) London, 1st Class Hons. Date of birth Sept. 2nd, 1912. (*Signed by*) E. D. Hughes, A. D. Scott, C. K. Ingold.

DRAKE, JACK WARD, "Oakwell View," Oxford Rd., Gomersal, nr. Leeds. English. I am a third-year student in the Honours School of Chemistry at Leeds University. I wish to become a member of the Society in order to keep in touch with modern chemical progress. Date of birth July 25th, 1914. (*Signed by*) H. M. Dawson, R. Spence, J. W. Baker.

ELLIOTT, ANTONY LESTER, 68, Rotton Park Rd., Edgbaston, Birmingham, 16. British. Student, Demonstrator in Pharmaceutical Chemistry. Chemist and Druggist. Date of birth May 15th, 1911. (*Signed by*) J. Newton Friend, Reece H. Vallance, J. Cooper Duff.

FISHER, SYDNEY JOHN MORTIMER, Rydal School, Colwyn Bay. British. Schoolmaster. B.A. and B.Sc. (Oxon.). A paper on "Acetonesulphonic Acid, etc.," recently submitted by Dr. Parkes for possible publication. Date of birth Aug. 20th, 1912. (*Signed by*) G. D. Parkes, S. G. P. Plant, D. Ll. Hammick.

FISK, NEIL REGINALD, 18, Bowood Rd., Clapham Common, S.W. 11. British. Freelance technical journalist (shall be editor of a monthly trade journal next month). Inter. B.Sc. Lond. Completed Final Hons. Course in Chemistry at University of London. 5½ years at Paint Research Station, Teddington (4½ years Assistant in Chemical Research Labs., 1 year Librarian). One year assistant editor of two monthly trade journals (one dealing with chemicals, one with food). (*Signed by*) Gerald Druce, J. Outram Cutter, L. A. Jordan, P. J. Gay, T. Hedley Barry.

GAUBERT, PETER, 36, Oxhey Rd., Oxhey, Herts. British. Student. B.Sc., A.R.C.S. (B.Sc. subject to satisfactory completion of a further year), Royal College of Science, London. Date of birth Sept. 20th, 1914. (*Signed by*) G. A. R. Kon, H. N. Rydon, R. P. Linstead.

HAYES, ALEXANDER HENRY, Helan Brae, Winifred Rd., Coulsdon, Surrey (Business: Hazlitt House, Southampton Buildings, W.C. 2). British. Technical Consultant and Editor. (Editor of "The Fuel Economist"). 27 years technical editing, and writing on metallurgy, combustion, water softening, steam, etc. (*Signed by*) Gerald Druce, Jules Cofman Nicoresti, Gabriel Cofman-Nicoresti.

HEBBS, LEWIS GOODIN SPIRE, Croy-Brae, Powys Lane, Broomfield Park, N. 13. British. Consulting Chemist. A.I.C. In Cross & Bevan laboratories for past fourteen years, and member of firm for last five years. (*Signed by*) C. Dorée, H. Lambourne, W. Taylor.

HOLMES, KENNETH EDWIN, 21, Fawcett St., West Brompton, S.W. 10. British. Research Student at Royal College of Science, London. B.Sc., London. 3½ years in Government Laboratory, London, as Assistant III (March 1932 to Sept. 1935). Date of birth Aug. 3rd, 1914. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, E. H. Farmer.

HUGHES, THOMAS PICTON, Bradford House, Llandovery, South Wales. British. Research Student. B.A. (Cambridge). Nat. Sci. Tripos, Part I, Class II; Part II, Class II, Div. I. Late Exhibitioner of Gonville and Caius College; Rhondda Student. Date of birth, Sept. 17th, 1914. (*Signed by*) Philip Bowden, T. M. Lowry, A. S. C. Lawrence.

HULSE, FRED, "Firdale," 33, Grove Rd., Halton, Leeds. British. Managing Director. 1913—1915, Chief Chemist with the Denaby & Cadeby Collieries, Ltd., working chiefly in connection with the prevention of gob fires and explosions. 1915—1919, Chief Chemist with Messrs. Brotherton & Co., Ltd., Stourton, Leeds. 1919 to the present time, Managing Director of F. Hulse & Co., Ltd., Woodlesford, Leeds. (*Signed by*) H. H. Hodgson, John Evans, James Bruce.

Irving, Harry Munroe Napier Hetherington, 2b, Crick Rd., Oxford. English. University Lecturer and Demonstrator in the Old Chemistry Department, Oxford. M.A., B.Sc., D.Phil. (Oxon.); A.I.C.; L.R.A.M. Sometime Lecturer in Organic Chemistry, The Queens College, Oxford; Tutor and Lecturer at St. Edmund Hall, Oxford; Head of the Science Department, the School of Arts, Crafts and Technology, Oxford, and University Lecturer and Demonstrator in the O.C.D. *J.C.S.*, 1929, 1038; **1930**, 87; **1931**, 751, 786, 1740, 2492; **1933**, 993, 142; **1934**, 325; **1935**, 90. Also papers in the *J.A.C.S.*, etc. (*Signed by*) F. D. Chattaway, D. Ll. Hammick, F. E. King.

Jarrett, Stanley Graham, 87, Stanmer Villas, Brighton 6, Sussex. British. Research Student at University College, London. B.Sc. (ext. London University) (1st Class). Holder of Brighton Technical College Leaving Schol., and the Henry Hallett Science Scholarship for Research Work in Organic Chemistry at University College, London. Date of birth Sept. 19th, 1914. (*Signed by*) O. L. Brady, E. D. Hughes, J. N. E. Day.

Jones, Griffith Glyn, 7, Arran Place, Ardrossan, Ayrshire. British. M.Sc. Cantab, B.Sc. Wales. Research Chemist, 1926—1935. Imperial Chemical Industries, (Explosives Group), Stevenston, Ayrshire. *J.C.S.*, 1926, **55**, 720; **1927**, 746. (*Signed by*) J. Weir, Norman Picton, A. G. White.

Kamthong, Bua, 51, Barkston Gardens, S.W. 5, at present 6, Heathfield Rd., Liverpool 15. *Siamese. Research Student. (B.Sc. Hons.) Liverpool.* Working for Ph.D. degree (Liverpool). (*Signed by*) *R. A. Morton, Wm. Doran, A. McGookin.*

McKenzie, Helen Mackay, 12, Irvine Place, Aberdeen. British. Research Chemist, Papermill. M.A., B.Sc., Aberdeen. Assistant Works Chemist (Paper Manufacture), 1930—1934. Assistant Research Chemist (Paper Manufacture), 1934 to date. Lecturer in Testing of Paper and Paper-making Materials, Robert Gordon's Colleges 1931 to date. (*Signed by*) Stephen R. H. Edge, R. Craven, Alex. Findlay.

Marsden, Ewart, 3, West View, Hipperholme, Halifax. British. Teacher. B.Sc. (London) 1917—1926, Assistant Chemist, British Dyestuffs Corporation. 1931—1935, Research Student. Desire to keep in touch with recent chemical developments. (*Signed by*) Herbert Henry Hodgson, Walter Fletcher, James Bruce.

Moignard, Lionel Arthur, Jesus College, Oxford. British. Research Student. B.A., Oxford. Engaged in research and desirous of keeping in touch with the literature. Date of birth Feb. 11th, 1914. (*Signed by*) J. C. Smith, D. L. Chapman, H. J. George.

Morgan, William McGillivray, 59, Church Rd., Gosforth, Newcastle-on-Tyne 3. British. Research Student. B.Sc. (Hons.) University of Durham, 1934. Demonstrator, Chem. Dept., Armstrong College, Newcastle (1934—1936). *J.C.S.*, **1935**, 1743. Date of birth Aug. 20th, 1913. (*Signed by*) G. R. Clemo, H. L. Riley, R. Raper, R. D. Haworth.

Morse, Gilbert Owen, 22, Chester Rd., Tottenham, N. 17. British. Research Student (Chemistry), Royal College of Science. B.Sc. (London, 1st Class), A.R.C.S. (Imperial College of Science, S.W. 7). Reason for desiring admission: to keep abreast of the advancement of chemistry. Date of birth, Dec. 4th, 1915. (*Signed by*) E. H. Farmer, B. Saunders, P. Winsor, J. S. Fitzgerald, C. H. Miller.

O'Neill, Leonard Alfred, 20, Shirland Rd., Maida Hill, W. 9. English. Research Chemist. B.Sc., M.Sc. (Queen Mary College, London). Investigation on "The Effect of One Salt on the Solubility of Another," *Trans. Faraday Soc.*, 1934, **30**, 12, 1134. Research Chemist to the Research Association of British Paint, Colour and Varnish Manufacturers. Date of birth Aug. 4th, 1913. (*Signed by*) J. Outram Cutter, D. R. Duncan, S. H. Bell.

Peill, Peter Livingstone Davies, "Chanctonbury," Oakdale, Southgate, N. 14. British. Research scholar. B.Sc., Lond. (External) (2nd Class Hons. in Special Chem.), A.I.C. Joseph Blamires Research Scholar in Colour Chemistry at Huddersfield Technical College, 1935 to date. Student at Brighton Technical College, 1931—1935. Date of birth April 17th, 1914. (*Signed by*) Herbert H. Hodgson, Gordon E. Watts, James Bruce.

Petrow, Vladimir A., 106, Edith Rd., West Kensington, W. 14. British. B.Sc., 1st Class Hons. Chem. (Lond.), A.I.C. Research Student. *J.C.S.*, **1934**, 1129 (with Dr. C. Dorée); **1935**, 1391 (with Dr. C. Dorée). Date of birth June 8th, 1914. (*Signed by*) J. C. Crocker, F. H. Lowe, C. Dorée, George S. Rolph.

Pitkethly, Robert Chalmers, 163, Tudor Avenue, Hampton-on-Thames, Middlesex. British. Student. B.Sc. (London), 1st Class, due after an additional year's study, A.R.C.S. (1st Class). Intermediate B.Sc. taken at school 3 years after Matriculation. Two years course for Final at the Royal College of Science. Date of birth Sept. 15th, 1915. (*Signed by*) H. J. T. Ellingham, Jocelyn Thorpe, E. H. Farmer.

RAWLINGS, ALAN ABRAHAM, 47, Spencer Place, Leeds 7, Yorks. British. Research Chemist. B.Sc. (1st Class Hons. Chemistry, 1934), Leeds University. 2nd year Ph.D. course in Organic Chemistry under Professor Challenger. Date of birth June 18th, 1914. (*Signed by*) Frederick Challenger, E. Rothstein, D. Ivor James, J. L. Stoves.

RAWLINSON, JOHN ALFRED, 24, Rosemary Gardens, Sheen Lane, East Sheen, S.W. 14. British. Chemist. 1928—1934, Research Chemist, Messrs. Colas Products, Ltd. From 1934 Assistant Chemist, Shell Marketing Co. Research work on colloid-chemical problems, particularly in connection with bitumens, soaps, and emulsions. (*Signed by*) J. Kewley, J. Kenyon, A. Houssa.

RAYNOR, GEOFFREY VINCENT, 28, Elm Tree Avenue, West Bridgford, Nottinghamshire. (Present address: 31, Warnborough Rd., Oxford.) British. Research Student. B.A. (Honour School of Chemistry, Oxford University). Date of birth Oct. 2nd, 1913. (*Signed by*) F. M. Brewer, G. D. Parkes, W. Hume-Rothery.

REASON, HAZEL ALDEN, 3, Wilderness Road, Onslow Village, Guildford. British. Secondary School Teacher. B.Sc. (Hons. Chem.), London University (Bedford College); M.Sc. (History Methods and Principles of Science, Pt. I). Private Study. Senior Science Mistress, County School for Girls, Guildford. At present studying for Pt. II, M.Sc. Access to Library required for seventeenth- and eighteenth-century publications on Chemistry. (*Signed by*) Phyllis V. McKie, Corona G. Trew, James F. Spencer.

RECORD, BASIL ROLAND, 9, Woodville Rd., Harborne, Birmingham. English. Research Student. B.Sc. (1st Class Hons.), Birmingham University. At present engaged on research work on "The Molecular Weight of Polysaccharide Derivatives by Osmotic Pressure Measurements." A summary of this work was given at the British Association Meeting (Norwich), 1935. (*Signed by*) W. N. Haworth, S. R. Carter, Wm. Wardlaw.

SHARMAN, IVAN MICHAEL, Kelvin Lodge, 1, Morella Rd., Wandsworth Common, S.W. 12. British. Laboratory Assistant to Government Chemist. Inter B.Sc. and subsidiary subject for B.Sc. (Spec.), London. Proceeding for B.Sc. (Special) Honours in Chemistry as an internal student of the University of London. Date of birth May 30th, 1914. (*Signed by*) J. Kenyon, R. Robertson, J. J. Fox, L. G. Groves.

SLATER, WILLIAM CHARLES, 4, Carlisle Avenue, E.C. 3. British born. Chemical manufacturer. Diploma of the City Guilds Technical College, Finsbury, in 1907. From 1907 to 1923 employed in various capacities as analytical chemist; since 1923 as a chemical manufacturer. (*Signed by*) C. Edwd. Sage, William H. Gough, R. Doumin.

SMITH, ARTHUR, 31, Lower Stanton Rd., Ilkeston. British. B.Sc., London. Teacher of Science. (*Signed by*) F. S. Kipping, E. B. R. Prideaux, B. D. Shaw, J. B. Firth, F. C. Laxton.

SMITH, JOHN CHAPMAN, 18, Francis Rd., Acocks Green, Birmingham. British. Student-demonstrator in Pharmaceutical Chemistry. M.P.S. (London). Date of birth May 16th, 1913. (*Signed by*) J. Newton Friend, Reece H. Vallance, J. Cooper Duff.

STILLER, ERIC THOMAS, 11E, Fawley Rd., Hampstead, N.W. 6. British. Research Chemist. B.Sc. (Glasgow); Ph.D. (St. Andrews). Researches in Carbohydrate Chemistry. Publications: *J. Amer. Chem. Soc.*, 1932, **54**, 1079, 1486. *J. Biol. Chem.*, 1933, **102**, 187; 1934, **104**, 299; **105**, 153; **106**, 421. *J.C.S.*, 1930, 2119. Part-author of "Textbook of Biochemistry," Saunders & Co., Philadelphia, 1935. (*Signed by*) Harold King, I. M. Heilbron, F. Fairbrother.

STYLE, DERRICK WILLIAM GRAHAM, King's College, Strand, W.C. 2. British. University Lecturer. B.Sc., Ph.D. (London). Teaching and Research at King's College since 1927. *J.C.S.*, 1930, 596, Allmand and Style. (*Signed by*) A. J. Allmand, Samuel Smiles, E. W. McClelland.

TIDD, ERNEST, 12, Raeburn Rd., Clarendon Park, Leicester. English. Research Student. B.Sc., 2nd Class Hons., Chem., University College, Nottingham, External, London. Am doing research in organic chemistry. Date of birth Oct. 14th, 1914. (*Signed by*) J. B. Firth, B. D. Shaw, F. C. Laxton, E. B. R. Prideaux, F. S. Kipping.

WAINWRIGHT, WILLIAM GLYN, 25, Astonmead, Aston, Hawarden, Chester. British. Research Student. B.Sc. (Hons.), Wales (1st Class Hons.). I wish to obtain the publications of the Chemical Society, and also to avail myself of the library facilities. Date of birth Dec. 16th, 1913. (*Signed by*) J. L. Simonsen, F. G. Soper, A. E. Bradfield.

WELDON, LEONARD HARVEY POCOCK, 9, Belsize Square, Hampstead, N.W. 3. English. Research Student. B.Sc., London (University College). To receive publications and use the Library. Date of birth July 5th, 1912. (*Signed by*) C. K. Ingold, C. G. Raison, C. L. Wilson.

WELLINGS, AUGUSTUS WILLIAM, 27, Acacia Rd., Leamington Spa, Warwickshire. English.

M.Sc. and B.Sc., University of Bristol. Researches on "Adsorption Indicators," published in *Trans. Faraday Soc.*, **1932**, and in the *Analyst*, **1933** and **1935**. Author of (i) "Chemical Symbols, Formulæ, and Calculations," (ii) "Volumetric Analysis" (both Methnen & Co.). Chemistry Master, Leamington College, since 1925. Vice-Principal, Leamington Evening Technical School since 1934. (*Signed by*) W. E. Garner, M. Nierenstein, M. Taylor.

Westmoreland-White, Beryl, "Menewethan," 99, Norfolk Avenue, Sanderstead, Surrey. British. Research Student. B.Sc. (London); A.R.C.S. Date of birth June 9th, 1912. (*Signed by*) James C. Philip, H. V. A. Briscoe, H. J. Emeléus.

Wilkinson, John Bernard, Lincoln College, Oxford. British subject. Undergraduate; reading for Honours Chemistry in University of Oxford. Date of birth Aug. 9th, 1916. (*Signed by*) N. V. Sidgwick, S. G. P. Plant, D. Ll. Hammick.

Wood, Frederick Charles, 20, South Farm Road, Worthing, Sussex. British. Research Chemist and Mycologist. B.A. (Hons.), Cambridge. I wish to keep in touch, *via* the Chemical Society, with latest chemical information. (*Signed by*) F. G. Mann, H. McCombie, F. B. Kipping.

Work, Thomas Spence, c/o Pearcey, 13, Montpelier Park, Edinburgh. Scottish. Research Student. B.Sc. (Hons. Chem.), Edinburgh. I am at present engaged in research under Professor G. Barger (since October 1934) and hold the post of demonstrator in his department. I have not yet published any papers on the work in which I am engaged. (*Signed by*) George Barger, Alex R. Todd, Alexander Lauder.

Forms of Recommendation for Fellowship accepted by the Council under Bye-Law 1 (2) :—

Doyle, Thomas Francis, 45, Belgrave Square, Rathmines, Dublin, S.W. 1. F.F.Sc., A.B.R.I. Irish. Chief Chemist, W. & R. Jacob & Co., Ltd., Biscuit Manufacturers, Dublin. With above firm since 1910 as Chief Assistant Chemist. Present position held since June 1934. Full Course Diploma Applied Chemistry, D.A.T.I., 1916. Foy Scholarship winner in Applied Chemistry. Member: S.P.A., S.C.I., American Chem. Soc. (*Signed by*) Frank Sykes.

Johnston, Henry Wyatt, 4048, Gage Rd., Montreal, P.Q., Canada. (Mailing Address: Officer in charge, Pulp and Paper Division, Forest Products Laboratories of Canada, 3420, University St., Montreal.) Canadian. Civil Servant. B.Sc. (Chem. Eng.), 1921, McGill University. M.Sc., 1927; Ph.D., 1929, McGill University. Chemist at Pulp and Paper Division since July 1929. Officer in charge since June 1934. (*Signed by*) G. S. Whitby, R. H. Manske.

Kinlay, Hugh Breen, c/o Messrs. Heynes Mathew, Ltd., P.O. Box 242, Cape Town, S.A. Temporary address: c/o Messrs. Davis and Soper, Ltd., 54, St. Mary Axe, E.C. 3. South African National, and therefore British subject. Chemist and Druggist. C. and D. (South Africa); M.P.S. (Gt. Brit.). I wish to become a Fellow of the Society in order to make use of Library whilst in London, also to obtain copies of Journal in order to keep abreast in advancement of chemical science. As a student was foundation member, Treasurer, and Chairman of Cape Peninsula Pharmaceutical Students Association. (*Signed by*) Charles Alex. Hill.

Oza, Suryakant Rupshanker, Dhrangadhra, Kathiawar, India, B.P. Hindu. Shift Manager, Shri Shakti Alkali Works. B.A. (Phys. & Chem.) and B.Sc. (Principle Chemistry) of Bombay University. Working in the above works for the last seven years. Worked as Assistant Chemist, Laboratory Superintendent, etc. Rose to the present responsible post. Carried out investigation and research work in Ammonia Soda Industry and allied subjects, such as Water Softening, Burning of Limestone, Ammonia Distillation and Absorption, Carbonation, Calcining, Brine Purification, Utilization of Waste and Effluent Liquors, over and above keeping general and technical control of the whole works. (*Signed by*) Kantilal M. Sheth.

Richardson, Albert S., The Procter and Gamble Co., Ivorydale, Ohio, U.S.A. United States. Director of Chemical Research, The Procter and Gamble Co. A.B., A.M., Ph.D., Princeton University. Publications include: "Detergent Value of Sodium Silicate," *Ind. Eng. Chem.*, **1923**, **15**, 241; "Some New Detergents," *Oil and Soap*, **1934**, **11**, 10. Joint publications include papers on fatty oils or soaps in *J. Am. Chem. Soc.*, **1924**, **46**, 157; *Ind. Eng. Chem.*, **1924**, **16**, 519; *ibid.*, **1925**, **17**, 80; *ibid.*, **1926**, **18**, 570; *ibid.*, **1932**, **24**, 1329; *Oil and Fat Ind.*, **1929**, **6**, No. 9, 19; *J. phys. Chem.*, **1929**, **33**, 1142. (*Signed by*) Frank C. Whitmore.

Ryland, Garnett, University of Richmond, Richmond, Virginia, U.S.A. American. Professor of Chemistry, Univ. of Richmond. M.A. (University of Richmond); Ph.D. (Johns Hopkins). Formerly Professor of Chemistry at the University of Maine and at Georgetown

College (Ky.). Author "Liquid Mixtures of Constant-Boiling Points," *American Chemical Journal*, Vol. XXII, *Chemical News*, Vol. 73. (*Signed by*) Walter A. Patrick.

SANDLER, EDGAR GEORGE, P.O. Box 2684, Capetown, Union of South Africa. British. Technical Representative for South Africa: The Trinidad Lake Asphalt Operating Company, Ltd. 1. As Technical Representative of the above-mentioned Company, the candidate is responsible for its engineering and chemical activities in South Africa. 2. Certificate of passing University of South Africa examination in Chemistry (1932). 3. Much interested and concerned with science of Chemistry, and now a part-time student of Advanced Chemistry at Capetown University. 4. Two Engineering Diplomas. (*Signed by*) D. C. Broom.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ATTWOOLL, A. W., and BROOME, D. C. Trinidad Lake asphalt. London 1935. pp. 56. ill. (*Recd.* 21/12/35.) From the Limmer & Trinidad Lake Asphalt Co.

BOMBAY. *Royal Institute of Science.* Second report (1926—1934). Bombay 1935. pp. iv + 73. ill. (*Reference.*) From the Principal.

LABORATOIRES DU BATIMENT ET DES TRAVAUX PUBLICS. (From *L'Entreprise Française*, 1935, 5.) pp. 195. ill. 50 *fr.* (*Recd.* 9/1/36.) From the Publishers: "L'Entreprise Française."

REMINGTON, JOHN STEWART. The paint laboratory note book: a handy guide to works practice. London 1935. pp. xii + 68. *ill.* 10*s.* (*Recd.* 6/1/36.) From the Publishers: Messrs. Leonard Hill.

SIEGEL, W. Die Verfahren der anorganisch-chemischen Industrie. Jahresberichte über die Patente und die technische Literatur der Industrieländer. Vol. I. Berichtsjahr 1934. Berlin 1935. pp. xvi + 501. ill. (*Reference.*) *M.* 34. From the Author.

II. *By purchase.*

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Cereal laboratory methods, with reference tables. 3rd edition. Omaha 1935. pp. viii + 204. ill. $3. (*Recd.* 23/12/35.)

AMERICAN SOCIETY FOR TESTING MATERIALS. Symposium on paint and paint materials. Philadelphia 1935. pp. vi + 150. $1.50. (*Recd.* 2/1/36.)

ANDREWS, ANDREW I. Enamels: the preparation, application, and properties of vitreous enamels. Champaign 1935. pp. xviii + 410. ill. $5.50. (*Recd.* 1/1/36.)

BHATNAGAR, S. S., and MATHUR, K. N. Physical principles and applications of magnetochemistry. London 1935. pp. xiv + 375. ill. 21*s.* net. (*Recd.* 19/12/35.)

BÖTTGER, W. [Editor.] Physikalische Methoden der analytischen Chemie. Part II. Leitfähigkeit, Elektroanalyse und Polarographie. Leipzig 1936. pp. xii + 343. ill. *M.* 28. (*Recd.* 17/12/35.)

BRAME, J. S. S., and KING, J. G. Fuel, solid, liquid and gaseous. London 1935. pp. xvi + 422. ill. 25*s.* net. (*Recd.* 23/12/35.)

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COMPTON, ARTHUR H., and ALLISON, SAMUEL K. X-rays in theory and experiment. 2nd edition of "X-rays and electrons." [New York] 1935. pp. xiv + 828. ill. *$7.50.* (*Recd.* 23/12/35.)

CREIGHTON, H. JERMAIN, and KOEHLER, W. A. Principles and applications of electrochemistry. 2 vols. New York 1935. pp. xviii + 502, xiv + 545. ill. $9. (*Recd.* 23/12/35.)

DOCZEKAL, RUDOLF, and PITSCH, HEINRICH. Absolute thermische Daten und Gleichsgewichtskonstante. Anleitung, Tabellen und Nomogramme zur praktischen Durchführung von Berechnungen. Wien 1936. pp. iv + 69. ill. *M.* 6.60. (*Recd.* 8/1/36.)

ELLIS, CARLETON. The chemistry of synthetic resins. 2 vols. New York 1935. pp. 1615. ill. $19.50. (*Recd.* 3/1/36.)

FINDLAY, ALEXANDER. Practical physical chemistry. 6th edition. London 1935. pp. xii + 318. ill. 8*s.* 6*d.* net. (*Recd.* 23/12/35.)

FRANCIS, FRANCIS. Notes on organic chemistry. London 1935. pp. viii + [264]. 12*s.* 6*d.* net. (*Recd.* 23/12/35.)

FRIEND, JOHN NEWTON. [Editor.] A textbook of inorganic chemistry. Vol. XI. Part iii. Derivatives of phosphorus, antimony and bismuth. By ARCHIBALD EDWIN GODDARD. London 1936. pp. xxviii + 318. (Two copies.) 20*s.* net.

HEERMANN, PAUL. Färberei und textilchemische Untersuchungen. 6th edition. Berlin 1935. pp. xii + 396. ill. *M.* 22.50. (*Recd.* 8/1/36.)

INTERNATIONAL CONGRESS OF SOIL SCIENCE, 3rd. Transactions. Vols. I and II. London

1935. pp. xii + 428, vi + 194. ill. (*Reference.*) 41*s*. net.

JÖRGENSEN, HOLGER. Die Bestimmungen der Wasserstoffionenkonzentration (p_H) und deren Bedeutung für Technik und Landwirtschaft. Dresden 1935. pp. xvi + 264. ill. *M.* 16. (*Recd.* 6/1/36.)

LAER, MARC H. VAN. La chimie des fermentations. Paris 1935. pp. 350. ill. 75 *fr.* (*Recd.* 30/12/35.)

McKIE, DOUGLAS, and HEATHCOTE, NIELS H. DE V. The discovery of specific and latent heats. London 1935. pp. 155. ill. 6*s*. net. (*Recd.* 23/12/35.)

OPPENHEIMER, CARL. Die Fermente und ihre Wirkungen. Supplement. Lieferung i, etc. Den Haag 1935 +.

RADLEY, J. A., and GRANT, JULIUS. Fluorescence analysis in ultraviolet light. 2nd edition. pp. xii + 326. ill. 21*s*. net. (*Recd.* 19/12/35.)

SEDLACEK, FRANZ. Auer von Welsbach. Wien 1934. pp. viii + 85. ill. *M.* 3.60. (*Recd.* 8/1/36.)

TREADWELL, F. P. Analytical chemistry. 8th edition. Vol. II. Quantitative analysis. Translated, enlarged and revised by W. T. HALL. New York 1935. pp. xiv + 858. ill. $6. (*Recd.* 23/12/35.)

WATERS, WILLIAM A. Physical aspects of organic chemistry. London 1935. pp. xvi + 501. 25*s*. *net.* (*Recd.* 19/12/35.)

III. *Pamphlets.*

BRITISH STANDARDS INSTITUTION. British standard specifications, No. 642—1935. Carbide of calcium (graded sizes).

—— —— No. 647—1935. Methods of testing glues. (Bone, skin, and fish glues.)

DEULOFEU, VENANCIO, and MENDIVE, JORGE R. Quimica de las vitaminas. Buenos Aires 1935. pp. 36.

DHAR, N. R. A new method of nitrogen fixation and conservation and reclamation of alkali lands. [Allahabad] 1935. pp. 46.

ELECTROCHEMICAL SOCIETY. Lithium: theoretical studies and practical applications. By HANS OSBORG. New York 1935. pp. 68. ill.

GODBOLE, N. N., and SADGOPAL, —. A comparative study of the utility of the milks and ghees, of the Indian cow and buffalo, as human food materials. Benares [1935].

HANNAH DAIRY RESEARCH INSTITUTE. Bulletin No. 6. An inquiry into the design, operation and efficiency of pasteurising plants. By A. W. SCOTT and NORMAN C. WRIGHT. Kirkhill 1935. pp. 72. ill.

INDIAN LAC RESEARCH INSTITUTE. Lac and the Indian Lac Research Institute. 2nd edition. Calcutta 1935. pp. x + 66. ill.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. Food and the consumer. By G. W. MONIER-WILLIAMS. London 1935. pp. 15.

—— Laboratory organisation. By LESLIE H. LAMPITT. London 1935. pp. 26. ill.

INTERNATIONAL TIN RESEARCH AND DEVELOPMENT COUNCIL. Technical Publications. Series A. No. 26. The mechanical properties of tin-base alloys. By D. J. MACNAUGHTAN and B. P. HAIGH. London 1935. pp. 12. ill.

UNITED STATES. *Department of Agriculture.* Technical Bulletin No. 485. Effects of particle size on the properties and efficiency of fertilizers. By A. L. MEHRING [and others]. Washington 1935. pp. 26. ill.

FORTHCOMING MEETINGS OUTSIDE LONDON.

BRISTOL.

95th Annual General Meeting and Anniversary Dinner.

Provisional Programme.

Thursday, April 16th, 1936.	3.45 p.m.	Tea in the Reception Room of the University.
	4.15 p.m.	Annual General Meeting in the large Lecture Theatre of the Department of Chemistry.
	7.30–8 p.m.	Reception by the President, and Anniversary Dinner in the Great Hall of the University.
Friday, April 17th, 1936.	10.30 a.m.	Hantzsch Memorial Lecture by Professor T. S. Moore, in the Lecture Theatre of the Department of Physics.
	1.0 p.m.	Lunch.
	2.30 p.m.	Inspection of work in the Departments of Chemistry and Physics.
		Visits—Particulars to be announced later.

GLASGOW.

Friday, February 7th, 1936, at 7.30 p.m. Lecture on " Some Recent Developments in Surface Action," by Professor E. K. Rideal, M.B.E., D.Sc., F.R.S., at the Royal Technical College.

LIVERPOOL.

Friday, February 7th, 1936, at 6 p.m. Lecture on " The Play of the Molecules in a Simple Chemical Reaction," by Professor H. M. Dawson, D.Sc., F.R.S., in the Chemistry Lecture Theatre of the University.

MANCHESTER.

Tuesday, February 4th, 1936, at 4.30 p.m. Joint Meeting with the University of Manchester Chemical Society. Lecture on " The Structure of Benzene," by Professor C. K. Ingold, D.Sc., F.R.S., in the Chemistry Lecture Theatre of the University.

Thursday, February 20th, 1936, at 7 p.m. Joint Meeting with the Manchester Sections of the Institute of Chemistry and the Society of Chemical Industry. Lecture on " Chemistry and Medicine," by Dr. J. F. Wilkinson, M.Sc., Ph.D., M.D., F.I.C., in the Lecture Theatre of the Manchester Central Library, St. Peter's Square.

Thursday, March 12th, 1936, at 7 p.m. A meeting for the reading of original papers in the Chemistry Lecture Theatre of the University.

NEWCASTLE AND DURHAM.

Friday, March 27th, 1936. Annual Dinner of the North East Coast Chemical and Allied Professions.

Fellows are invited to attend the Thirty-Third Bedson Lecture to be held in the Chemistry Lecture Theatre, Armstrong College :—

February, 1936, at 6.30 p.m. Lecture on " The Application of X-ray Diffraction to Chemistry," by Mr. J. D. Bernal, M.A. (Date not yet fixed.)

NORTH WALES.

Friday, February 7th, 1936, at 8 p.m. Lecture on " Ergot and Ergotism," by Professor G. Barger, M.A., D.Sc., F.R.S., in conjunction with the University College Chemical Society, in the Chemistry Lecture Theatre, University College, Bangor.

ST. ANDREWS AND DUNDEE.

Friday, February 28th, 1936, at 5 p.m. Joint meeting with St. Andrews University Chemical Society. Lecture on " The Chemistry of the Sesquiterpenes," by Professor J. L. Simonsen, D.Sc., F.R.S.

SHEFFIELD

Saturday, February 8th, 1936, at 2.30 p.m. Joint Meeting with the Yorkshire Branch of the Science Masters' Association in the Chemistry Lecture Theatre of the University.

2.30–4.0 p.m. *Discussion on "The teaching of new ideas in chemistry in school and university." Attention will be directed to three topics:* (1) valency, (2) electrolytic dissociation, (3) indicators.

4.0–4.30 p.m. Tea.

4.30–6.30 p.m. Inspection of exhibits and experimental demonstrations in the University Chemical Laboratories.

Friday, March 13th, 1936, at 5.30 p.m. Lecture on "Carbohydrates," by Professor W. N. Haworth, D.Sc., F.R.S., in the Chemistry Lecture Theatre of the University.

FORTHCOMING MEETINGS IN LONDON.

Thursday, February 6th, 1936, *at* 8 *p.m.*

Ordinary Scientific Meeting, at which the following papers will be read :—

"1 : 2 : 3-Triketotetramethyl*cyclo*pentane : A Blue Triketone." By C. W. Shoppee.

"Electrolytic Reduction of Organic Compounds. Part I. Analogies between Cathodic Reduction and the Action of Dissolving Metals. Reduction of Sorbic Acid." By E. Isaacs and C. L. Wilson.

"Some Points Arising from the Modern Theories of Corrosion. Part I. Waterline Corrosion." By J. E. O. Mayne.

Wednesday, February 12th, 1936, *at* 5.30 *p.m.*

Sixteenth Faraday Lecture entitled "Radioactivity and Atomic Theory," by The Rt. Hon. Lord Rutherford of Nelson, O.M., F.R.S., in the Lecture Theatre of the Royal Institution, Albemarle Street, London, W. 1.

Thursday, February 20th, 1936, *at* 8 *p.m.*

Joint discussion with the Faraday Society on "The Kinetics of Gaseous Combustion," to be opened by Dr. R. G. W. Norrish, B.A., followed by Professor W. A. Bone, Dr. H. F. Coward, Professor W. E. Garner, and Mr. C. N. Hinshelwood.

Thursday, March 5th, 1936.

Extraordinary General Meeting at 7.45 p.m., to consider a proposal by the Council for the alteration of the Bye-Laws, notice of which was sent to Fellows resident in the United Kingdom on January 29th, 1936.

Ordinary Scientific Meeting, at 8 p.m.

Thursday, March 19th, 1936, *at* 8 *p.m.*

Joint discussion with the Biochemical Society on "The Chemistry and Biochemistry of Lipoids."

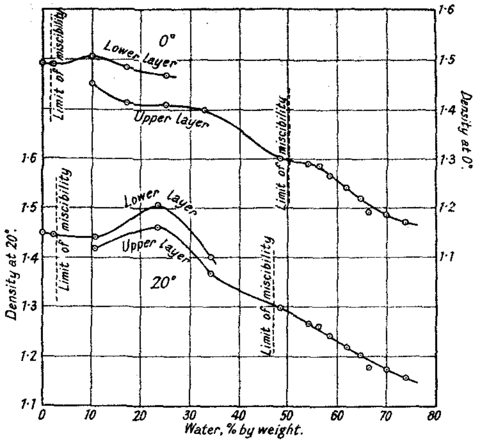
INSTITUTE OF FUEL.

A meeting of the Institute of Fuel will be held in the Meeting Room of the Chemical Society on Thursday, February 13th, 1936, at 6 p.m., when a paper on "The Co-ordination of Fuel and Power Supplies of Great Britain" will be present by Mr. O. W. Roskill. Fellows are invited to attend the meeting, and advance proofs can be obtained from the Secretary of the Institute of Fuel, 58, Victoria Street, London, S.W. 1, after February 6th.

KEY INDUSTRY DUTY (PARACETAMINOPHENOL).

An announcement has been received from the Board of Trade that representation has been made for the exemption of paracetaminophenol from the duty imposed by Section 1 of the Safeguarding of Industries Act, 1921. Any communication should be addressed to the Principal Assistant Secretary, Industries and Manufactures Department, Board of Trade, Great George Street, S.W. 1, within one month from the 23rd of January, 1936.

FIG. 3.



Densities at 0° and 20° of mixtures of nitrogen peroxide and water.

TABLE I.

Miscibility of Nitrogen Peroxide and Water.

(Percentages by weight.)

Total	Lower layer.			Upper layer.		
H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.
			At 20°.			
2·8	Separation into two layers begins.					
9·55	44·8	54·1	1·0	18·7	49·0	32·3
15·41	47·8	51·0	1·2	15·0	48·1	36·9
19·02	49·7	48·1	2·2	12·6	46·0	41·0
24·45	55·4	42·3	2·3	12·8	44·8	43·4
30·00	63·7	33·8	2·5	12·8	43·3	43·8
34·81	67·10	28·5	4·4	12·4	41·6	45·9
36·40	—	—	—	13·7	39·4	46·9
40·52	70·3	27·1	2·6	18·5	37·2	44·3
47·0	Separation into two layers ends.					

Total	Lower layer.			Upper layer.		
H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.
			At 0°.			
1·8	Separation into two layers begins.					
5·01	43·12	55·87	1·07	12·31	57·52	30·17
10·35	46·24	52·36	1·40	9·94	53·68	36·38
14·97	48·53	50·94	0·53	9·63	50·19	40·18
19·59	51·81	46·01	2·18	10·21	48·77	41·02
19·91	53·32	44·67	2·01	10·03	47·51	42·46
24·84	55·28	42·89	1·83	10·13	45·46	44·41
29·58	57·51	40·02	2·48	10·70	41·93	47·39
34·39	59·80	38·81	1·39	11·23	40·08	48·69
39·51	62·98	34·10	2·92	14·27	35·10	50·63
45·31	63·84	31·22	4·94	17·16	31·94	50·90
50·1	Separation into two liquid layers ends.					

TABLE II.

Miscibility of Nitrogen Peroxide and Water at 0°.

(Molecular percentages.)

Total,	Lower layer.			Upper layer.		
H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.
8·56	Separation into two layers begins.					
21·22	49·76	45·37	4·92	6·87	22·50	70·63
37·10	51·93	41·40	6·67	4·94	18·76	76·30
47·34	56·00	41·37	2·63	4·49	16·48	79·03
55·42	55·46	34·67	9·87	4·69	15·78	79·53
55·96	57·18	33·72	9·10	4·51	15·03	80·47

Total	Lower layer.			Upper layer.		
H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.	N_2O_3, %.	N_2O_5, %.	H_2O, %.
62·73	59·30	32·39	8·31	4·46	14·09	81·45
68·20	59·81	29·30	10·89	4·46	12·30	83·24
72·80	64·33	29·38	6·29	4·59	11·53	83·88
76·95	63·41	24·17	12·42	5·65	9·78	84·57
80·90	59·87	20·61	19·42	6·75	8·85	84·40
84·87	Separation into two liquid layers ends.					

TABLE III.

Densities of Homogeneous Liquids.

H_2O, %.	Temp.	*d.*	$d^{0°}$.	$d^{20°}$.
73·9	− 3·6°	1·17335	1·1705	1·1560
	+ 19·45	1·15690		
70·0	− 11·60	1·19380	1·1845	1·1705
	+ 17·94	1·17335		
66·4	− 26·10	1·21018	1·1910	1·1765
	− 1·65	1·19380		
	+ 25·65	1·17335		
64·7	+ 10·21	1·21018	1·2179	1·2010
	+ 20·12	1·20184		
	+ 31·0	1·19380		
61·9	− 2·49	1·24081	1·2381	1·2190
	+ 16·29	1·22255		
	+ 29·78	1·21018		
58·5	+ 5·0°	1·25732	1·2621	1·2415
	+ 14·7	1·24680		
	+ 20·01	1·24081		
56·2	− 20·40	1·30590	1·2822	1·2600
	− 9·30	1·29286		
	+ 15·45	1·26608		
54·1	− 17·7	1·30590	1·2885	1·2647
	− 6·2	1·29286		
	+ 18·8	1·26608		
50·5	+ 20·19	1·29286		

TABLE IV.

Densities of Two Liquid Phases.

(*a*) At 0°.			(*b*) At 20°.		
H_2O, %.	Upper layer.	Lower layer.	H_2O, %.	Upper layer.	Lower layer.
0	—	1·49250	0	—	1·44750
2·15	—	1·49029	2·15	—	1·44450
10·12	1·44988	1·50508	10·67	1·41784	1·43914
17·23	1·41171	1·48256	23·48	1·46011	1·50308
25·32	1·40831	1·46690	34·17	1·36581	1·39881
32·98	1·39734	—	48·31	1·29622	—
48·31	1·29893	—			

at room temperature (about 14°) was slightly less than that of the non-aqueous layer, but that when the mixture was warmed in the hand and shaken, the densities of the layers were reversed, and the acid layer sank to the bottom. The point of inversion is therefore at a lower concentration of water than that recorded for very narrow tubes by Heberlein.

EXPERIMENTAL

Preparation and Separation of the Mixtures.—(i) *At* 20°. The mixtures were made up by weight in the separator shown in Fig. 4. This consisted of a cylindrical vessel *S*,* 20 cm. long and 1—2 cm. wide, into which three tubes were sealed, *viz.*, a central filling tube A_0 at the top, and two lateral "drawing-off" tubes B_1 and B_2, the former reaching nearly to the bottom of the central tube and the latter to within about 1 cm. of the bottom. These tubes were connected to two bulbs, D_1 and D_2, for collecting the two liquid phases. The connecting tubes and taps are shown in the figure. Since substantial pressures, ranging from 1 to 3 atm., were developed in the separator, the taps C_1 and C_2 were held firmly in position with elastic bands. They were lubricated with a little Apiezon L grease, but in later experiments this was replaced by the phosphoric acid lubricant used by Daniels and Verhoek (*J. Amer. Chem. Soc.*, **1931**, **53**, 1250).

The requisite amount of water was weighed out in a pyknometer, the delivery tube of which was drawn out into a long fine capillary for insertion down A_0. By blowing gently down the short arm of the pyknometer, the water could be caused to syphon over. The pyknometer was then withdrawn and again weighed, thus giving the weight of water taken.

The water in the separator was frozen in liquid air, and the separator sealed on to the nitrogen peroxide filling apparatus at *N* (Part II, Fig. 2 inset), through a constriction, and exhausted. A weighed quantity of nitrogen peroxide was then distilled over from the weighing tube *W* of the filling apparatus into the separator *S*, and the latter was finally sealed off under vacuum at the constriction.

With the taps C_1 and C_2 fully open, the contents of the separator were allowed to warm to room temperature very slowly, since any sudden change of pressure in the apparatus caused the liquid to be forced up the inner tubes into the two bulbs D_1 and D_2. Before commencing the separation, it was frequently necessary to clear the two inner tubes B_1 and B_2 from mixtures of the two liquid phases. This was effected by closing the taps C_1 and C_2, and warming the bulbs D_1 and D_2 by hand to force the liquid out of the tubes.

* The first separator was of uniform width throughout; a second was wider in the upper half.

The separator was then immersed as far as possible in a thermostat at 20°, and kept for at least an hour before the separation was started. The lower layer was first drawn off into the bulb D_1 by arranging the separator so that D_1 came outside the thermostat, and closing the tap C_1; D_1 was then cautiously cooled by bringing a Dewar flask of liquid air near it, and the difference of pressure caused the lower layer to be forced up B_1 and over into D_1. As soon as the upper layer was seen to be rising in B_1, the tap C_1 was opened to equalise the pressure and stop the transference of liquid. The upper layer was then similarly drawn off into D_2, the process being stopped by opening the tap C_2, whilst the excess of liqnid remained in the central tube. Some practice and great care were necessary in order to obtain homogeneous samples of the two layers.

Finally, D_1, D_2, and the central reservoir of the separator were immersed simultaneously (in order to avoid distillation) in three small Dewar flasks of liquid air and, when the contents were completely frozen, the two bulbs D_1 and D_2 were sealed off at the constrictions provided.

FIG. 4.

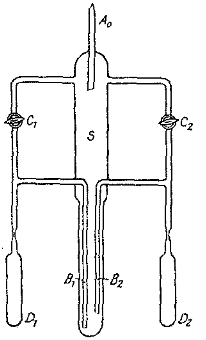
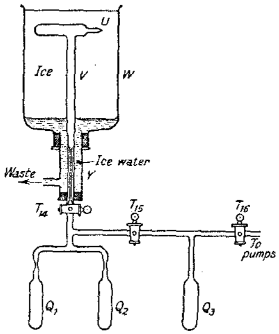


FIG. 5.



(ii) *At* 0°. The separator described above proved unsuitable for use at 0°, and was replaced by another (see Fig. 5). The vessel, V, in which the mixtures were prepared consisted of a cylindrical bulb of about 30 c.c. capacity attached to a tube 12 cm. long and terminating in a wide capillary 10 cm. long, closed at the far end by a tap T_{14}. The mixtures were prepared, as described above, with the cylindrical bulb in a vertical position. A known amount of water was first introduced through the tube U and frozen; U was sealed to the nitrogen peroxide filling apparatus at N (Part II, Fig. 2 inset), through a constriction, a known weight of nitrogen peroxide was introdnced, and the vessel was sealed off. The contents of the bulb were then allowed to become warm and mix thoroughly.

The separator was mounted in an ice-bath, but the tap T_{14} was left outside the bath, as shown in Fig. 5. The bulbs Q_1, Q_2, Q_3 were then sealed on below the tap. The vessel V was surrounded by washed and crushed ice, while the glass tube Y, through which the capillary was observed, was maintained at 0° by keeping it filled with ice-water from the bath above. This precaution was found to be essential, since any inequality of temperature produced violent disturbance of the liquids in the capillary and rendered separation impossible.

The mixture was maintained at 0° for at least ½ hour before the separation was started. The part of the apparatus below T_{14} was then exhausted, and tap T_{16} closed. The mixed liquids in the capillary were first removed by cooling the bulb Q_3 in liquid air and cautiously distilling the contents of the capillary into it by opening tap T_{14}. When the capillary was occupied exclusively by the homogeneous lower layer, tap T_{15} was closed, and a sample of the lower layer was distilled into Q_1 by cooling it in liquid air. Tap T_{14} was then closed, and the bulb Q_1 sealed off at the constriction. In a similar manner, a sample of the homogeneous upper layer was sealed off in Q_2.

The method of separation employed at 0° had the advantage that the liquids were adequately protected from temperature disturbances and could be controlled satisfactorily; moreover, the line of demarcation between the two layers could be very readily observed in the capillary; finally, the interposition of a tap between the main bulk of liquid and the sample to be frozen obviated any risk of distillation during the freezing of the samples.

Chemical Analysis of the Mixtures.—The analytical results are expressed in terms of the components H_2O, N_2O_3, and N_2O_5. The total nitrogen and the total tervalent nitrogen were determined directly by chemical analysis, their difference giving the quinquevalent nitrogen. The weight of water was obtained by subtracting the combined weights of N_2O_3 and N_2O_5 from the total weight of the sample analysed.

The method of analysis first tried consisted in dissolving the sample in excess of standard alkali and determining the total nitrogen by back titration with standard acid, the tervalent nitrogen being estimated by titration with $N/10$-permanganate (Lunge and Berle, *Z. angew. Chem.*, 1906, **19**, 807; Raschig, *ibid.*, 1905, **18**, 1281); but, when the method was tested on pure nitrogen peroxide, it was found, in agreement with Lunge and Berle, that the nitrite value was about 5% too low. These investigators attributed this discrepancy to oxidation of the nascent nitrite by atmospheric oxygen, since they obtained the theoretical result only when the absorption was carried out in an atmosphere of nitrogen. A more probable explanation is that of Sanfourche (*Compt. rend.*, 1922, **175**, 469), *viz.*, that nitric oxide is produced in the reaction with water and is then oxidised by the atmospheric oxygen. Satisfactory results with pure nitrogen peroxide were, however, obtained by using a second method, described by Lunge and Berle (*loc. cit.*) and by Marchlewski (*Ber.*, 1891, **24**, 3271).

In this method the samples are absorbed in concentrated sulphuric acid, and (i) the total nitrogen is estimated as nitric oxide by the Lunge nitrometer, while (ii) the tervalent nitrogen is again determined by titration with permanganate. A typical test analysis with 0·001524 g.-mol. of pure nitrogen peroxide gave by (i) 0·001526 g.-mol. and by (ii) 0·001533 g.-mol.

To carry out the analysis, a fine scratch was made on the neck of the bulb containing the sample, and the whole weighed. The sample was then allowed to come to equilibrium at 20° or 0°, and suddenly frozen in liquid air. The neck of the bulb was then cracked open at the scratch, care being taken to retain every piece of glass for future weighing, and the bulb was dropped into a small (200 c.c.) flask containing about 100 c.c. of concentrated sulphuric acid. The flask was immediately stoppered with a tightly fitting cork thinly coated with paraffin wax. On melting, the frozen sample dissolved immediately in the sulphuric acid, and after a few minutes a colourless solution was obtained. This was transferred to a graduated flask and made up to the mark with more concentrated sulphuric acid, all washing of the absorption flask and small bulb being effected with this agent. The small bulb was washed free from acid, dried, and weighed, together with the end which had been cracked off, thus giving the weight of the sample taken for analysis. The total nitrogen was determined by shaking a known portion of the sulphuric acid solution with mercury in a Lunge nitrometer and measuring the nitric oxide produced. It was found that theoretical results could only be obtained if the sulphuric acid solution was diluted with water to about 80% acid before use in the analysis. The tervalent nitrogen was determined by running the acid solution into $N/10$-permanganate at 40° from a burette with its tip just below the surface of the permanganate, in order to prevent volatilisation of the nitrous acid (Lunge, *Ber.*, 1877, **10**, 1075).

Measurements of Density.—(a) *Flotation.** The floats (about 15 mm. long and 2 mm. in diameter) were made from thin-walled tubing of Pyrex glass, closed at one end and melted down to a solid tail at the other; they were kept for some months before being calibrated, in order to diminish the strain in the glass (Turner and Cousen, J., 1928, 2654). Twenty-six floats were adjusted to give increments of density varying from 0·006 to 0·039 between 1·15 and 1·6, and were calibrated in mixtures of toluene and bromoform.

For determining the densities of the mixtures of nitrogen peroxide and water, three floats were placed in a tube about 12 mm. in diameter and 12 cm. long. Known amounts of water and of nitrogen peroxide were introduced as described above, and the vessel was then sealed off and allowed to become warm. The density became steady after a few hours, but the mixtures were usually allowed to stand over-night before observations were begun. Flotation temperatures above 0° were observed in a water-bath, but for temperatures below 0° the bath consisted

* Compare Richards and Shipley, *J. Amer. Chem. Soc.*, 1914, **36**, 1; Richards and Harris, *ibid.*, 1916, **38**, 1000; Robinson and Briscoe, J., 1926, 70; Robinson and Smith, *ibid.*, p. 1262; Lowry and Jessop, J., 1929, 1421.

of an unsilvered Dewar flask containing ether, which was cooled to the required temperature by cautious addition of carbon dioxide snow to the well-stirred liquid.

Some 40 readings were taken of each flotation temperature, and the densities of each mixture at 0° and 20° were then deduced by graphical interpolation.

(b) *Capillary pyknometer.* In order to determine the densities in systems containing two liquid phases, a sample of each layer was sealed off in a capillary pyknometer tube by the method described above. After being kept over-night, the tube containing the sample was immersed in a thermostat at 20° with the tapered end downwards. After an hour, a fine mark was made on the glass at the level of the meniscus, and the process was repeated at 0° by immersing the tube in a bath of washed crushed ice. The tube was then dried and weighed, its contents transferred to the rounded end, and frozen in liquid air. The tube was broken open at a fine scratch made with a sharp glass knife, a perfectly clean fracture being obtained in all cases; the two portions of the tube were then washed, dried, and weighed, thus giving the weight of the sample. The portion with the rounded end was than discarded, and the weight of water filling the other portion to each of the fine marks was determined. From these data, the density of the sample at 0° and 20° could be calculated. On account of the smallness of the volumes of liquid handled, it was necessary to exercise great care in adjusting liquid levels and in weighing, and observations were repeated a few times wherever possible.

SUMMARY.

1. The compositions of the two liquid layers formed in mixtures of nitrogen peroxide and water have been determined by analysis.

2. The limits within which two liquid layers are formed in the system H_2O–N_2O_3–N_2O_5 at 0° and 20° have been plotted on triangular diagrams.

We are indebted to the Imperial Chemical Industries, Limited, for maintenance grants (to E. L. and W. V. L.) during the period in which this research was carried out.

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4. *The Hydrolysis of Arylsulphuric Acids.* Part I.*

By G. NORMAN BURKHARDT, W. G. KENNETH FORD, and ERIC SINGLETON.

POTASSIUM phenylsulphate is readily hydrolysed by boiling dilute mineral acid: $SO_2(OPh)(OK) + H_2O \longrightarrow Ph{\cdot}OH + KHSO_4$ (I), but is stable in boiling aqueous solution containing acetic acid and sodium acetate, and also to alkalis up to 150° (Baumann, *Ber.*, 1878, **11**, 1907; Burkhardt and Lapworth, J., 1926, 684). The isomeric potassium nitrophenylsulphates have been shown to be much more readily hydrolysed by mineral acid than either potassium phenylsulphate or the isomeric potassium tolylsulphates (Burkhardt and Wood, J., 1929, 141). The hydrolytic fission of arylsulphates appears, therefore, to be of special interest in that, although it is catalysed by hydrogen ions, yet it is accelerated by the presence of electron-attractive (proton-repulsive) groups in the aromatic nucleus. Also, because substituted phenols can often be prepared more readily than, *e.g.*, the corresponding benzyl chlorides, carboxylic acids, aldehydes, or ketones, the hydrolysis of their sulphuric esters should prove useful in the study of the influence of molecular constitution on reactivity in cases when difficulties of synthesis have limited the use of reactions involving these other materials. The possibility of carrying out the hydrolysis of potassium arylsulphates in water instead of in aqueous alcohol or other mixed solvent is one of the factors which lead to the absence of side reactions in this case.

The hydrolyses were followed, at 48·6° and at temperatures near 80°, by titrating, with alkali, the potassium hydrogen sulphate formed according to equation (I), starting with solutions $M/12$ with regard to potassium arylsulphate and $M/24$ to hydrochloric acid. Potassium phenylsulphate and *p*-nitrophenylsulphate were shown to be salts of strong acids, for, with hydrochloric acid, they had no buffering action detectable by indicator methods in concentrations up to those used in the hydrolysis; potassium sulphate

* Strictly, aryl hydrogen sulphates; but the historical name is retained.

in similar concentrations showed marked buffering action. If it is assumed, from these observations, that all the potassium arylsulphates which have been examined may be regarded as salts of strong acids, the reaction is represented by equation (II):

$$\begin{array}{l} R{\cdot}O{\cdot}SO_2{\cdot}O' + H^{\cdot} + H_2O + K^{\cdot} + Cl' = R{\cdot}OH + HSO_4' + H^{\cdot} + K^{\cdot} + Cl' \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \uparrow\downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad H^{\cdot} + SO_4'' \end{array} \quad . \quad . \quad . \quad . \quad (II)$$

In accordance with this equation, the reaction is of the first order with regard to arylsulphate, and partially autocatalytic in virtue of the increase in hydrogen-ion concentration due to the partial dissociation of the HSO_4' ion formed in the hydrolysis. Satisfactory velocity constants were obtained as described by Burkhardt, Evans, and Warhurst (Part II, succeeding paper), the value of 0·01 being used for the second dissociation constant of sulphuric acid. This corresponds with that found by Dawson, Pycock, and Spivey (J., 1933, 291) in their experiments on the hydrolysis of ethyl acetate in salt-free solution at 25°, and proved sufficiently accurate for the present purpose. Velocity constants were calculated from the expression $k_1 = (dx/dt)/(a + p)(b - x)$, where a and b are the initial concentrations of acid and arylsulphate (mols. per litre) respectively, x is the increase in total acid ($KHSO_4$ produced) in time t (secs.), and p the increased concentration of hydrogen ions due to the dissociation of the acid formed in the hydrolysis.

Up to half reaction and in the concentrations used, the values of $(a + p)$ obtained by this method correspond closely with the dissociation of a fixed fraction of the potassium hydrogen sulphate produced according to equation (I), and for the standard concentrations used, good constants were also obtained using the integrated form of the equation $dx/dt = k_2(a + x/5{\cdot}5)(b - x)$, *viz.*, $k_2 = [2{\cdot}303/t(a + b/5{\cdot}5)] \log b(a + x/5{\cdot}5)/a(b - x)$. The agreement of the constants obtained by these two methods was satisfactory; *e.g.*, for potassium phenylsulphate at 48·6°:

Reaction, %	12·5	18·75	25	37·5	50
$k_1 \times 10^5$ (tangents)	8·83	8·93	9·00	9·00	9·03
$k_2 \times 10^5$ (approximate expression)	8·58	8·68	8·85	8·88	8·95

It is now clearly established that the actual rates of reactions, involving suitably related substances and measured under similar conditions chosen on grounds of convenience, are directly related to certain features of the molecular structures of the reactant molecules in a manner which can be expressed in terms of the electronic theories. This applies to substances showing quite small differences in velocity constants in certain cases, including a very wide range of reactions involving groups attached to the benzene ring or to side chains in aromatic compounds. Table I contains the data for a comparison of the velocity constants for the hydrolysis of the substituted phenylsulphates with those for a number of other reactions. The close qualitative relationships are clearly shown. The values relative to each phenomenon rise or fall consistently down each column except those shown in parentheses, most of which relate to *o*-substituted compounds, to which special considerations are known to apply. Comparisons with other reactions are shown in the subsequent discussion of the quantitative relationships (Figs. 1 and 2).

The complete phenylsulphate series (B and C) show clearly that the sulphate group is most readily hydrolysed when it is attached to a position of low electron-availability, and that the rate of hydrolysis decreases with rising electron-availability at the various positions in benzene derivatives (reactions of Class B, Ingold, *Ann. Reports*, 1927, **24**, 155). It is therefore clear that the substituents are not acting in virtue of their influence on the interaction of the phenylsulphate ion and the oxonium ion. This applies whether the reaction proceeds by the type of mechanism represented in equation (III) or by that in (IV), either of which would give a bimolecular form involving phenylsulphate and hydrogen-ion concentrations.

$$Ph{\cdot}O{\cdot}SO_2{\cdot}O' + H_3O^{\cdot} \longrightarrow Ph{\cdot}OH + H_2SO_4 \qquad (III)$$

$$Ph{\cdot}O{\cdot}SO_2O' + H_3O^{\cdot} \rightleftarrows Ph{\cdot}O{\cdot}SO_2{\cdot}OH + H_2O \longrightarrow Ph{\cdot}OH + H_2SO_4 \qquad (IV)$$

(Both these are followed by the equilibria $H_2SO_4 \overset{H_2O}{\rightleftharpoons} H_3O^{\cdot} + HSO_4' \overset{H_2O}{\rightleftharpoons} H_3O^{\cdot} + SO_4''$.)

TABLE I.

A.	B. k (48·6°).	C. k (78·7°).	D. –CO·NH₂.	E. –CO·NH₂.	F. –CH₂Cl.	G. –CO₂Et.
p-NO_2	44·5	12·0	245	6300	7·4	5090
o-NO_2	35·8	8·8	(5·6)		8·4	
m-NO_2	20·5	5·8	204	5200	9·0	3110
m-Cl	16·3				23·7	363
(*o*-OMe)	13·3	4·53				
o-Cl	13·0	4·42	(33·3)	(489)	36	
p-Br	11·5		204	1800	50	242
p-Cl	10·8	3·62	(208)	1800	62	212
m-OMe	10·2	3·40				59
H	8·9	3·35	(217)	944	100	40
m-Me	8·8	3·20	201	752	139	35
o-Me	7·75	2·72	(22·7)	(50·5)	484	
p-Me	6·87*	2·38*	183	623	1060	23
p-OMe	4·50	1·80	131	462		10·5

* The authors are indebted to Mr. C. Horrex and Miss D. Jenkins for these values.

Col. A. The substituents are arranged in the order of their influence on the phenylsulphate hydrolysis.
,, B. Velocity constants ($\times 10^5$) at 48·6° for the hydrolysis of the substituted phenylsulphates.
,, C. ,, ,, ($\times 10^3$) at 78·7° ,, ,, ,, ,, ,, calculated from measurements at various temperatures from 76·7° to 82·5°.
,, D. Velocity constants ($\times 10^4$) at 100° (time in mins.) for the acid hydrolysis of the substituted benzamides (Reid, *Amer. Chem. J.*, 1900, **24**, 403).
,, E. As D, but for alkaline hydrolysis.
,, F. Relative velocity constants for the hydrolysis of the substituted benzyl chlorides (CH_2PhCl = 100) at 83° (Olivier, *Rec. trav. chim.*, 1923, **42**, 775; Olivier and Berger, *ibid.*, 1927, **46**, 605).
,, G. Velocity constants ($\times 10^4$) at 30° (time in mins.) for the alkaline hydrolysis of the substituted ethyl benzoates (Kindler, *Annalen*, 1926, **450**, 1; 1927, **452**, 90).

In (III), electron-attractive (proton-repulsive) substituents in the phenylsulphate would resist combination with the oxonium ion, and in (IV), such groups would tend to increase the dissociation and thereby reduce the concentration of the intermediate neutral complex. Hence, the substituents must be regarded as acting mainly by their effect on other factors in the molecular breakdown by either mechanism. A similar conclusion applies to the acid hydrolysis of substituted benzamides (D). The phenylsulphate breakdown apparently involves the fission of the oxygen–sulphur bond (V) and *not* the carbon–oxygen bond (VI) because, with phenylsulphates, no phenylating properties have been detected analogous to the alkylating properties of the alkylsulphates (VII) which indicate carbon–oxygen breakdown in that series. The well-known difficulty of breaking the bond between the aromatic nucleus and oxygen makes this mechanism probable. On the other

Ph·O⋮SO_2·OK (V.)

Ph⋮O·SO_2·OK (VI.)

Et⋮O·SO_2·OK
Ph·NH⋮H (VII.)

hand, alkaline hydrolysis, which is observed at 100° with *o*- and *p*-nitrophenylsulphates only (Burkhardt and Wood, *loc. cit.*) and is much slower than any of the acid hydrolyses, may take place by the fission of the carbon–oxygen bond in a reaction analogous to the alkaline hydrolysis of *o*- or *p*-chloronitrobenzene.

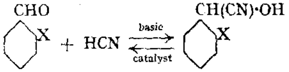
In that it is catalysed by hydrogen ions and yet accelerated by electron-attracting substituents, the acid hydrolysis of substituted benzamides is analogous to the phenylsulphate hydrolysis, but it contrasts with this in showing most marked steric effects when *o*-substituents are present (Table I). The alkaline hydrolyses of benzamides and benzoic esters are also subject to typical strong steric effects. The benzyl chlorides resemble the phenylsulphates in that the *o*-substituents considered here show little or no steric effect (Olivier, *Rec. trav. chim.*, 1926, **45**, 296). In all these reactions the bond next but one to the nucleus is broken (VIII*a*, *b*, *c*, *d*), and this differentiation into strongly and slightly sterically hindered classes is significant. In the former class, the approach of the ion or molecule of the other reactant to the atom next to the nucleus is clearly involved, and as it appears that even small *o*-substituents always make this more difficult, the other cases

apparently do not require such a mechanism as part of the rate-regulating process. In the case of the benzyl chlorides, the ionisation of the halogen which regulates the rate

Ph—CH_2—¦—Cl	Ph—O—¦—SO_2—OK	Ph—CO—¦—OEt	Ph—CO—¦—NH_2
(VIII*a*.)	(VIII*b*.)	(VIII*c*.)	(VIII*d*.)

should be independent of the approach of water to the methylene group (compare Polanyi and Ogg, *Trans. Faraday Soc.*, 1935, **31**, 604), and similarly, the mechanism of the phenylsulphate hydrolysis would appear not to involve the attack of the reagent on that part of the sulphate group which is within the sphere of steric influence of small *o*-substituents.

It must be noted, however, that this conclusion is rendered less certain by the demonstration by Lapworth and his collaborators that steric hindrance cannot be satisfactorily regarded as a simple obstruction phenomenon in the *o*-substituted benzene derivatives. Lapworth and Manske (J., 1928, 2533) showed that an abnormally high percentage of cyanohydrin was formed in the equilibrium between *o*-substituted benzaldehydes and hydrogen cyanide (IX) in spite of the necessity for the attachment of the cyanide ion to the carbonyl carbon atom. This indicated that the influence of *o*-substituents on these



(IX.)

equilibria could not be treated on the classical lines (Flürscheim, J., 1909, **95**, 718), and it was suggested that direct interaction between the two *o*-groups must be involved. In continuation of this work, Mr. Glyn Owen and others (unpublished) have shown that the formation of cyanohydrins is also abnormally *fast* with *o*-substituted benzaldehydes. This imposes a hitherto unsuspected reservation on the application of steric considerations to kinetics, and the results of a study of steric effects on the arylsulphate hydrolysis will be communicated shortly.

Quantitative Relationships.—In Fig. 1 it is shown that some of the relationships represented in Table I are remarkably quantitative (Burkhardt, *Nature*, 1935, **136**, 684). As abscissæ are plotted the logarithms of the dissociation constants of a series of substituted benzoic acids, so that these act as a reference series for the other phenomena, and as ordinates the logarithms of the velocity constants for four of the reactions represented in Table I in which the organic reactants contain the same substituents as the benzoic acids with which they are being compared. The straight-line relationship is fully supported or these phenomena although the larger deviations are all beyond experimental error and their significance will require separate discussion. The choice of the dissociation constants of the benzoic acids as reference series is arbitrary, but it shows that the velocity relationships which could have been illustrated against a velocity reference series can also be quantitatively related to ionisation equilibria.

Hammett and Pfluger (*J. Amer. Chem. Soc.*, 1933, **55**, 4079) observed a similar relationship between the dissociation of various carboxylic acids and the rate of reaction of their methyl esters with trimethylamine, $R{\cdot}CO_2Me + NMe_3 \longrightarrow R{\cdot}COO'\}NMe_4{}^{\cdot}$, but they considered the reaction exceptional in showing this relationship.* In that they were able to include, on a single straight line, the constants for aliphatic and *o*-substituted aromatic acids and esters as well as *m*- or *p*-substituted derivatives, their conclusion was well sub-

* Since this paper was written and a summary published (Burkhardt, *Nature, loc. cit.*), Hammett (*Chem. Reviews*, 1935, **17**, 125) has extended the scope of the relationship observed by him and Pfluger (*loc. cit.*) to include a wide variety of pairs of closely related phenomena, including, as one pair, the logarithms of the dissociation constants of the substituted benzoic acids against the logarithms of the rates of hydrolysis of the benzoic esters (curve E, Fig. 1). Since he stresses closely related phenomena, the present extension to include reactions less clearly related on *a priori* grounds is largely complementary to his, and requires a still wider explanation. Each of the curves in Fig. 3 provides another example of the type of relationship which he discusses.

stantiated. It has, however, been widely recognised that *o*-substituents in the aromatic series, and particularly α- and β-substituents in the aliphatic series, bring in quite special factors * operating to very different degrees in different reactions. It therefore becomes reasonable to consider, first, *m*- and *p*-substituted derivatives, and for these the linear logarithmic relationship is found to hold between a wide variety of reactions and consequently would appear to have a more general significance than follows from its application to a single pair of closely related phenomena.

Watson and his collaborators have plotted, against the dipole moments of monosubstituted benzene derivatives, the logarithms of both the dissociation constants of the benzoic and phenylacetic acids containing the same substituents, and those of velocity constants (or derived activation energies) for a variety of side-chain reactions (Nathan and Watson, J., 1933, 893, 1248; Evans, Morgan, and Watson, J., 1935, 1174; Dippy and Watson, *J. Soc. Chem. Ind.*, 1935, **54**, 735). Smooth curves were obtained for the majority of *m*-derivatives, and their form is very similar for the different phenomena. This is in accord with the existence of a direct relationship between the logarithms of the different velocity and dissociation constants for these *m*-derivatives.

To illustrate further the application of the linear logarithmic relationship, a number of other reactions are represented in Fig. 2 against the same reference series as was used in Fig. 1. The curve (H) for the hydrolysis of the substituted cinnamic esters, considered in conjunction with that for the benzoic esters (G) in Fig. 1, shows that the same influences from the substituents operate on the hydrolysis of the carbethoxyl group with the same relative effectiveness as compared with one another, whether the group is attached directly to the benzene nucleus or separated from it by the CH:CH group in the cinnamic side-chain. The slope of curve G being 2·5 and that of curve H 1·25, it can be stated that the introduction of the CH:CH group into the side-chain diminishes the effectiveness of *m*- and *p*-substituents by 50%. For the same reaction (hydrolysis of the carbethoxyl group by alkali) measured in the two series at the same temperature, this conclusion appears to be satisfactory in the unqualified form.

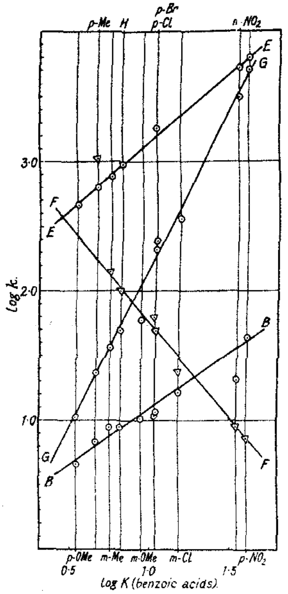
The iodine–chlorine interchange (curve I) brings in yet another type of reaction and a further indication of the persistence of the quantitative relationship at the end of a side chain, which in this case is saturated. The dissociation constants of the phenylacetic acids (curve K; all the other curves represent velocities) indicate the same persistence of the relationship along a side chain and its application to another dissociation equilibrium. The bromination of acetophenones (J) and the acid hydrolysis of the benzamides (D) are representative of reactions for which the straight-line relationship apparently fails: the former curve has a minimum at the *m*-nitro-derivative (or, alternatively, *p*-nitroacetophenone constitutes the sole anomaly), and the latter shows a marked **S** form which occurs also, but less markedly, in the phenylsulphate points (B, Fig. 1). Many reactions may be expected to deviate farther still. In general, reactions and particular substituents which have required special treatment on the simpler forms of electronic theory will fail to fall on straight lines when plotted against any of the phenomena which show the linear relationship. Shoppee (J., 1931, 1225), discussing a group of such reactions, plotted the free-energy change in the benzaldehydecyanohydrin equilibrium (Lapworth and Manske, *loc. cit.*) against the logarithms of the velocity constants for the alkaline hydrolysis of the benzoic esters (Kindler, *loc. cit.*) and obtained a smooth curve with a maximum.

The results given in Figs. 1 and 2 show that the linear logarithmic relationship is of very wide application in the case of *m*- or *p*-substituted derivatives, and in its simplest form, it is clearly much more satisfactorily applicable to remote substitution, of which the *m*- and *p*- cases have been most extensively studied, than to other types of structural change. The present communication is primarily concerned with this type of substitution, but a few preliminary observations on the further applicability of the logarithmic relationship may be recorded.

* As was emphasised above (p. 20), these factors are more complex than a simple steric hindrance. They include, *e.g.*, chelation and resonance phenomena, which are often peculiar to groups close to one another.

In a number of cases, similar plots of the logarithms of velocity constants against those of dissociation constants give, for the limited data available, straight lines for

FIG. 1.



Ordinates for curves.

B . . . *log* (k × 10⁵) *for acid-catalysed hydrolysis of the substituted potassium phenylsulphates at* 48·6°.

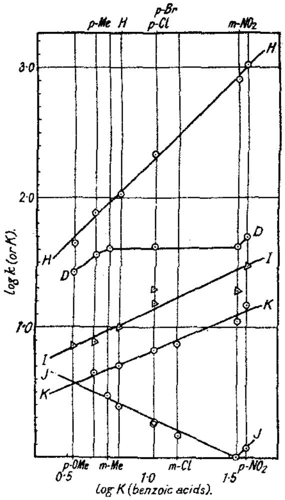
E . . . *log* (k × 10⁴) *for alkaline hydrolysis of the substituted benzamides at* 100° (*Reid*).

G . . . *log* (k × 10⁴) *for alkaline hydrolysis of the substituted ethyl benzoates at* 30° (*Kindler*).

F . . . *log* k *for hydrolysis of the substituted benzyl chlorides by aqueous alcohol at* 83° (*Olivier*).

Abscissæ: *log* K (*benzoic acids*) . . . *logarithms of the dissociation constants* (× 10⁵) *of the substituted benzoic acids, taken from Landolt–Börnstein or International Critical Tables except the values for o- and p-chloro- and p-bromo-benzoic acids* (*Dippy and Williams*, J., 1935, 343).

FIG. 2.



Ordinates for curves.

H . . . *log* (k × 10³) *for alkaline hydrolysis of the substituted ethyl cinnamates at* 30° (*Kindler*).

D . . . *log* (k × 10⁴) *for acid hydrolysis of the substituted benzamides at* 100° (*Reid*).

I . . . *log* (k × 10³) *for reaction* $KI + C_6H_4X{\cdot}S{\cdot}[CH_2]_2{\cdot}Cl$ *in acetone at* 55° (*Baddeley and Bennett*, J., 1933, 261).

J . . . *log* (k × 10) *for bromination of substituted acetophenones at* 25° (*Evans, Morgan, and Watson*).

K . . . *log* (K × 10⁵) *of the substituted phenylacetic acids* (25°) (*Dippy and Williams*, J., 1934, 161, 1888).

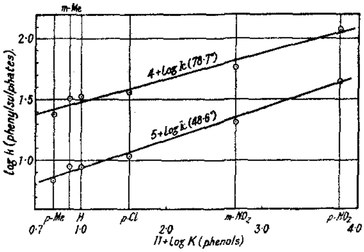
o-derivatives, but these are displaced from the *m*-, *p*-curves by amounts corresponding to the effects peculiar to the *o*-derivatives, and major deviations are commoner than in the *m*-, *p*-series; *e.g.*, the abnormally high rate of hydrolysis of potassium *o*-methoxy-

phenylsulphate * and the abnormally low dissociation constant of *o*-phthalaldehydic acid will lead to anomalies in any plot involving either of these two substances. In relating reactions which are similarly or not markedly affected by factors due to the close proximity of the groups, curves for *m*- and *p*-derivatives should be found to include the *o*-derivatives also.

Apart from closely related phenomena such as those compared by Hammett and Pfluger, it appears that changes of structure such as have been studied in the aliphatic series do not commonly give similar linear relationships. Some examples give smooth non-linear curves which can be interpreted, but others show no simple relationship at all.

In considering the physicochemical explanation of the linear relationships, it is convenient to examine phenomena as closely related as possible, as did Hammett and Pfluger. Fig. 3 shows the relationship between the logarithms of the rates of hydrolysis of the substituted potassium phenylsulphates at two temperatures and the logarithms of the dissociation constants of the corresponding phenols. Here the points lie somewhat closer to the straight line than those in the benzoic acid reference series in Fig. 1; particularly is this true of the points for the *m*-nitro-derivatives. Similar though smaller deviations are to be noticed with *m*-nitro-derivatives in Fig. 2, and a consideration of the removal

Fig. 3.



of anomalies by altering the reference series provides one approach to the explanation of the larger deviations from the linear relationships.

We are indebted to Professor Polanyi for drawing our attention to the explanation of the relationship between the rates of the acid-catalysed hydrolysis of the phenylsulphates and the dissociation of the corresponding phenols provided by the discussion of Horiuti and Polanyi (*Acta Physicochemica, U.R.S.S.*, 1935, **2**, 505).

The curve in Fig. 3 corresponding to the higher temperature is the less steep, as is to be anticipated if substitution mainly affects the activation energy, the slopes being 0·26 at 48·6° and 0·21 at 78·7°, a fall of 20% for a rise of temperature from 321·6° to 351·7° Abs. This variation complicates the use of slopes as a measure of the sensitivity of a reaction to substitution (compare p. 21), and an examination of the significance of the linear relationship in terms of energetics is required to elucidate this problem.

It may be noted that the results for the substituted potassium phenylsulphates given in Table II (derived from the constants to two temperatures by the application of the Arrhenius equation, $k = \alpha e^{-E/RT}$) indicate fairly definitely a rise in α from the most rapidly hydrolysed derivatives to the slowest, and a corresponding fall in the temperature-sensitive term, the effect of changes in the activation energy predominating (Burkhardt, *J. Inst. Chem.*, 1933, 301).

* This is the only anomaly in the phenylsulphate series. The value is anomalous whether it is considered from the point of view of the electronic theory, or on analogies with other isomerides and the influence of methoxyl in other reactions, or as it concerns the linear relationship. No explanation has been established. The effect might be accounted for by (*a*) the basicity of the methoxyl group, (*b*) the stabilisation of a single bond between the groups, or (*c*) direct interaction of the two groups.

TABLE II.

Substituent.	p-NO_2.	o-NO_2.	m-NO_2.	o-Cl.	p-Cl.	m-OMe.	H.	m-Me.	o-Me.	p-Me.	p-OMe.
$k_{48 \cdot 6^{\circ}} \times 10^6$	44·5	35·8	20·5	13·0	10·8	10·2	8·9	8·8	7·75	6·80	4·50
E (kg.-cals.)	24·7	23·8	24·8	26·2	26·2	26·1	27·0	26·7	26·5	26·6	27·4
$\alpha \times 10^{-14}$	0·24	0·06	0·18	0·10	0·30	0·68	2·4	1·5	0·88	0·79	2·3

The analysis in terms of the Arrhenius equation, which is developed elsewhere, follows the current methods. On the other hand, the existence of the linear logarithmic relationship and a parallelism between the α and the E terms (compare Burkhardt, *Nature, loc. cit.*) suggests a direct consideration of the influence of substitution on the logarithms of velocity and equilibrium constants, *i.e.*, on free energies (Burkhardt, *ibid.*). According to the transition-state method, as used by Evans and Polanyi (*Trans. Faraday Soc.*, **1935**, **21**, 875) or by Wynne-Jones and Eyring (*J. Chem. Physics*, **1935**, **3**, **492**), the velocity constant of a reaction is determined by the equilibrium between the initial and the transition state; log k (velocity) is directly related to the free-energy change in this process as log K (equilibrium) is to the total free-energy change in dissociation, and the linear relationships described above may be stated as follows in terms of the transition-state conception.

The influence of substituents on the free-energy changes associated with the equilibria between the initial and the transition states, in the reactions considered in respect of velocity, are directly proportional to their influence on the free-energy changes between the initial and the final states in corresponding dissociations.

These relationships may be regarded as developments from Flürscheim's observation of the parallelism between the influence of substituents on aromatic substitution and on the dissociation of the corresponding benzoic acids (J., **1909**, **95**, 725). Most of the data which have been used here have been accounted for on a qualitative basis, either in terms of Flürscheim's theory of valency or, more completely, in terms of the electronic theory which has incorporated the essentials of the earlier view. One of the modifications of the latter treatment which is required by the recognition of their quantitative nature may be stated as follows: Substituents operate with the same relative effectiveness, as compared one with another, on all the phenomena connected by the linear relationship. It is improbable that the temporary effects, to which the substituents may give rise, would influence all the reactions proportionately, and it therefore appears that such effects are not important in those cases where the relationship is followed closely, although they may provide the explanation of some of the individual deviations. In these cases the polarisability of a substituent would only be effective in so far as it became a polarisation in the course of any particular reaction.

The hydrolysis of the potassium arylsulphates and a number of problems concerning the quantitative relationship between reaction velocities and equilibria will be discussed further in the near future.

EXPERIMENTAL.

Velocity Measurements.—10 C.c. of $N/4$-hydrochloric acid were added to 50 c.c. of an $N/10$-aqueous solution of the substituted potassium arylsulphate in a well-stoppered flask in a thermostat ($\pm$ 0·03° at 48·6°, $\pm$ 0·05° at about 80°), both solutions having attained the temperature of the bath before mixing. As soon as possible and also at suitable intervals, samples were removed, run on to ice, and titrated with $N/10$- or $N/20$-alkali, p-nitrophenol being used as indicator and the alkali being standardised in a blank experiment on each occasion. The hydrolyses were carried out at least in duplicate. The delivery jets of the pipettes were bent back into an elongated S alongside the bulb, so that the latter was largely immersed in the thermostat liquid when the meniscus was set; with a standard procedure to regulate drainage, this was satisfactory for the present series of experiments. The pipettes were calibrated at the temperatures concerned. The initial concentration of the acid was obtained by extrapolating the curve back to zero time, that of the phenylsulphate being deduced from the volumes and concentrations of solutions and in some cases checked by complete hydrolysis.

The phenols for the preparation of sulphates were all purchased except m-chlorophenol, which was prepared from m-chloroaniline by diazotisation. The b. p. or m. p. of each was checked, and where necessary the phenol was purified by distillation or crystallisation. The

substituted potassium phenylsulphates were prepared by the method of Burkhardt and Lapworth (*loc. cit.*), except that the temperature of the reaction mixture was kept below 35° for the *m*-methyl and the methoxy-derivative to avoid sulphonation (therefore in these cases the solvent was not distilled off), and for the nitro-derivatives Burkhardt and Wood's modification (*loc. cit.*) was used. The products were recrystallised from water or aqueous alcohol, and examined qualitatively for inorganic sulphate and chloride and for the free phenol. Analysis for potassium gave molecular weights within 0·5% of theory in all cases.

To obtain an estimate of the strength of the phenylsulphuric acids, 10 c.c. of $N/4$-hydrochloric acid were added slowly to 25 c.c. of $N/10$-solutions of potassium phenylsulphate, *p*-nitrophenylsulphate, or sulphate and of distilled water, and the p_H values of the solutions were taken at various stages by the B.D.H. capillator. The potassium sulphate showed appreciable buffering; the others were indistinguishable.

The authors thank Mr. C. Horrex and Miss D. Jenkins for determining the rates of hydrolysis of potassium *p*-tolylsulphate, Mr. Glyn Owen for permission to refer to unpublished work (p. 20), and Imperial Chemical Industries Ltd. for a grant.

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5. *The Hydrolysis of Arylsulphuric Acids. Part II. Kinetic Considerations.*

By G. Norman Burkhardt, Alwyn G. Evans, and Ernest Warhurst.

In conjunction with the work described in Part I (preceding paper), the influence of variations in the concentration of the acid catalyst on the hydrolysis of a typical potassium arylsulphate was examined, and a method for obtaining velocity constants for these reactions developed.

Potassium *p*-tolylsulphate was used for these experiments. Different samples were prepared separately, purified, and tested according to the methods given in Part I. Apart from concentrations and temperature conditions, the procedures for the hydrolysis and measurements were also the same. The hydrolysis is represented in equation II of Part I ($R = C_6H_4Me$), and, with the symbols used therein, we have for the autocatalysed reaction

$$dx/dt = k(a + p)(b - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The values of a and b were obtained as in Part I; as before, the value 0·01 was used for the second dissociation constant of sulphuric acid, and this was applied to obtain values of p from the equation

$$(p + a)p/(x - p) = 0{\cdot}01 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The slopes of the curves for the graph of x against t were measured by taking tangents at various points up to 75% reaction, and the constants were obtained from equations (1) and (2).

In these experiments, 10 c.c. of hydrochloric acid of known concentration ($N/20$, $N/10$, $N/4$) were added to 50 c.c. of $N/10$-potassium *p*-tolylsulphate when both solutions had reached the temperature of the thermostat (80·5°). The constants obtained (see below) are independent of the hydrochloric acid concentration for this range and within the accuracy of these experiments. The mean value (0·00287 at 80·5°) gives 0·00237 when reduced to 78·7° by use of the activation energy (26,600 cals.) given in Part I. This is in good agreement with the value (0·00238) recorded there.

Concn. (N) of HCl added	0·05	0·10	0·10	0·25	0·25	0·25
k (mean) $\times 10^3$	2·73	2·76	2·75	2·85	2·95	2·93

When the hydrolysis is half completed, the concentration of the HSO_4' ion exceeds that of the hydrogen ion except in the experiments with $N/4$-acid. From the constancy of the values of k, obtained at different stages of the hydrolyses, both in these experiments (see below) and by the same method in the preceding paper, it is clear that the HSO_4' ion has

little or no effect on this reaction, in contrast to the hydrolysis of ethyl acetate (Dawson, Pycock, and Spivey, J., 1933, 291).

Hydrolysis, %	21·6	32·0	38·9	42·4	52·8
$k \times 10^3$	2·78	2·70	2·72	2·73	2·72

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6. *The Thermal Interaction of Deuterium and Ammonia.*

By Adalbert Farkas.

A comparison of the rates of certain reactions involving light and heavy hydrogen not only permits us to deduce conclusions with regard to the general theory of chemical change, but also affords a possibility of using heavy hydrogen as an indicator in elucidating the mechanism of complicated processes. We can also study a whole group of chemical reactions involving no other process than an exchange of hydrogen atoms, $H + XD \rightleftharpoons XH + D$.

Before the discovery of heavy hydrogen the thermal conversion of para- into ortho-hydrogen was the only example of this type of reaction: $H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H$ (A. Farkas, *Z. Elektrochem.*, 1930, **36**, 782; *Z. physikal. Chem.*, 1930, *B*, **10**, 419), the exchange of hydrogen atoms, otherwise undetectable, being traceable by this process.

The homogeneous interaction between light and heavy hydrogen, involving the reactions $H + D_2 \rightleftharpoons HD + D$, $D + H_2 \rightleftharpoons HD + H$, was dealt with in a previous paper (A. and L. Farkas, *Proc. Roy. Soc.*, 1935, *A*, **152**, 124); and the present paper concerns the exchange reaction between deuterium and ammonia which takes place in the gas phase above 600°.

Experimental.

The experimental arrangement was practically the same as that already described (*idem, ibid.*).

A silica reaction vessel (vol. 68 c.c.) was heated in an electric furnace, the temperature of which was measured by a platinum–platinum-rhodium thermocouple. The ammonia and deuterium were mixed in the reaction vessel by admitting a certain pressure of each gas; then from time to time small samples of gas (0·003 c.c. at *N.T.P.*) were abstracted from the vessel by means of a capillary lock, and their deuterium contents analysed by the micro-thermo-conductivity method (A. Farkas, *Z. physikal. Chem.*, 1933, *B*, **22**, 344; A. and L. Farkas, *Proc. Roy. Soc.*, 1934, *A*, **144**, 467) after the ammonia had been frozen out.

To detect any possible catalysis by the walls of the reaction vessel, the rate of the para-hydrogen reconversion was measured and found to be the same (within the limits of experimental error) as that reported previously. Furthermore, the behaviour of heavy hydrogen and ammonia separately in the reaction vessel was investigated. With the former, scarcely any change was found in the deuterium content during 1 or 2 hours at the temperature at which the exchange experiments with ammonia were done, showing that an exchange reaction with hydrogen adsorbed or absorbed on the walls was negligible. With ammonia alone in the reaction vessel, its decomposition was investigated by measuring the amount of the uncondensable gas formed: at all temperatures the velocity of decomposition was negligible when compared with the exchange reaction, and therefore the amount of hydrogen and nitrogen formed did not affect the accuracy of the analysis of the deuterium content; *e.g.*, at 794° and 59 mm., the amount of ammonia decomposed in 36 minutes was only 5%, forming about 5 mm. of uncondensable gas, whereas the half-life period of the exchange reaction was found to be a few minutes at the same temperature (cf. p. 28).

In the first experiments the equilibrium between light and heavy hydrogen and light and heavy ammonia was determined. The complete equilibrium between the seven molecular species H_2, HD, D_2, NH_3, NH_2D, NHD_2, and ND_3 is given by the equations

$$H_2 + D_2 \rightleftharpoons 2HD \quad (1)$$

$$2NHD_2 \rightleftharpoons NH_2D + ND_3 \quad (2)$$

$$2NH_2D \rightleftharpoons NHD_2 + NH_3 \quad (3)$$

$$NH_3 + HD \rightleftharpoons NH_2D + H_2 \quad (4)$$

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Assuming classical distribution of the H and D atoms in the equilibria (1), (2), and (3), such that

$$K_1 = [HD]^2/[H_2][D_2] = 4 \quad (5)$$
$$K_2 = [NHD_2]^2/[NH_2D][ND_3] = 3 \quad (6)$$
$$K_3 = [NH_2D]^2/[NHD_2][NH_3] = 3 \quad (7)$$

then the equilibrium constant

$$K_4 = [NH_2D][H_2]/[NH_3][HD] \quad (8)$$

which defines the equilibrium for low deuterium concentrations is identical with the expression

$$K_4 = 3[H/D]_h[D/H]_a/2 \quad (9)$$

where $[H/D]_h$ and $[H/D]_a$ denote the ratio of the hydrogen to the deuterium content for hydrogen and ammonia respectively.

This type of isotopic equilibrium was first treated by Urey and Rittenberg (*J. Chem. Physics*, 1933, **1**, 137), and it was shown that, owing to the different zero-point energies, masses, moments of inertia, etc., of the isotopic molecules involved, the equilibrium constant would in general differ from unity, corresponding to equipartition, a value which is, however, reached at higher temperatures. For instance, the equilibrium constant of the reaction $HD + H_2O \rightleftharpoons HDO + H_2$, *viz.*, $K = [HDO][H_2]/[H_2O][HD]$, which is 2·9 at 20°, falls to 1·2 at 450° (L. and A. Farkas, *Trans. Faraday Soc.*, 1934, **30**, 1071).

FIG. 1.

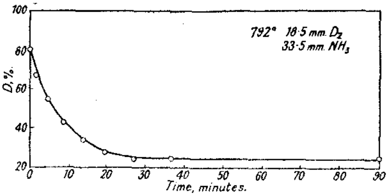


Fig. 1 shows the attainment of the equilibrium at 792° between 18·5 mm. D_2 (80%) and 33·5 mm. NH_3. In Table I the measurements are summarised, the equilibrium deuterium content of the ammonia, D_a, being calculated according to

$$D_a = (D_0 - D_h)2P_{D_2}/3P_{NH_3} \quad (10)$$

the significance of D_0 and D_h being clear from the table headings.

TABLE I.

Temp.	NH_3 press., mm. (P_{NH_3}).	D_2 press., mm. (P_{D_2}).	Original % D (D_0).	D, %, at equilibrium. In hydrogen (D_h).	In ammonia (D_a).	$[H/D]_h[D/H]_a$.
808°	49	59	80	35	36	1·04
820	38	57	80	37	43	1·28
750	66	66	80	32	32	1·00
710	55	56	80	34	37	1·14
792	33·5	18·5	80	24	21	0·84
788	26	26	88	34	36	1·09
					Mean	1·05

In these experiments the equilibrium is practically reached when the deuterium contents of the hydrogen and ammonia have become equal, *i.e.*, when $D_h = D_a$ or $[H/D]_h[D/H]_a = 1$ (or perhaps slightly higher).

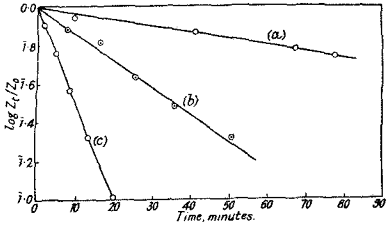
In evaluating the following experiments, the value was assumed to be 1·00, i.e., equilibrium was regarded as established when

$$P_{D_2}D_0 = (P_{D_2} + 1{\cdot}5\,P_{NH_3})D_h \quad (11)$$

The progress of the exchange reaction with time can be represented by $Z_t = Z_0e^{-k't}$, where $Z_t = D_t - D_h$ and $Z_0 = D_0 - D_h$ denote the excess concentrations of deuterium relative to

equilibrium at times t and 0 respectively, and k^* is a constant depending on pressure and temper ature. Fig. 2 shows that this relation is obeyed with some accuracy, the graphs of log Z_t/Z_0 against time being linear. From these lines, the half-life τ of the exchange reactions was deter mined, *i.e.*, the time required for Z_t to become halved; τ is related to k^* by the depression $\tau = (\log_e 2)/k^*$, and it is used to characterise subsequent reaction rates.

FIG. 2.



(*a*) 681°, 22 mm. D_2 + 72 mm. NH_3.
(*b*) 730°, 16 mm. D_2 + 54 mm. NH_3.
(*c*) 792°, 18·5 mm. D_2 + 33·5 mm. NH_3.

The dependence of the velocity on the pressures of ammonia and deuterium was investigated at 680—790°, with the following results:

Variation of deuterium pressure.

Temp.	p_{D_2}.	p_{NH_3}.	τ, mins.
680°	10	207	45
680	21	191	38
681	22	185	48
680	40	207	47
682	65	208	45
727	16	114	15
727	17	95	18
727	31	106	19
725	40	86	20
722	107	105	15
790	4	22	6·2
788	26	26	6·2

Variation of ammonia pressure.

Temp.	p_{D_2}.	p_{NH_3}.	τ, mins.
681°	22	72	86
679	19	137	58
681	22	185	48
681	22	191	38
680	21	373	33
730	16	20	48
730	15	54	22
727	20	76	17
727	17	95	18
730	16	114	15
725	14	177	12
726	17	200	11
794	10	17	8
792	18·5	33·5	6

Alteration of the deuterium pressure over a range of 10—100 mm. did not appreciably affect τ, but increase of ammonia pressure decreased it.

From the dependence of reaction rate on temperature (see below), the apparent energy of activation (A) was calculated to be 62 kg.-cals. by means of the formula $1/\tau = \text{const.} \times e^{A/RT} \times 1/\sqrt{T}$, where the factor $1/\sqrt{T}$ is due to the fact that the concentration of the reactants is proportional to $1/T$ at constant pressure and that the number of collisions is proportional to $\sqrt{T}$.

Temp.	p_{D_2}.	p_{NH_3}.	τ, mins.
681°	22	72	86
727	20	76	17
792	19	72	3

In Table II the rates of the exchange reactions between D_2 and NH_3 and between D_2 and H_2 are compared, the times of half change for the latter reaction (col. 5) being calculated on the basis of Farkas and Farkas's data (*loc. cit.*). In the temperature range 900—1000° Abs., the former reaction proceeds 30—40 times more slowly (col. 6) than the latter at the same temperature and pressure (col. 7; see p. 33).

TABLE II.

Temp.	p_{D_2}.	p_{NH_3}.	τ, mins.	τ, mins., for $H_2 + D_2$ reaction.	Ratio.	k_I/k_{II}.
788°	26	26	6·2	0·21	30	29
722	107	105	15	0·58	26	25
722	20	20	50	1·45	37	36
720	51	55	31	1	31	30
681	22	22	210	5·2	40	39

DISCUSSION.

There are four possible mechanisms for the interchange between ammonia and deuterium:

$$\text{I.}\ \begin{cases} NH_3 = NH_2 + H \\ D_2 = D + D \\ NH_2 + D = NH_2D \\ H + D = HD \end{cases} \qquad \text{III.}\ \begin{cases} D_2 = D + D \\ D + NH_3 + M = NH_3D + M \\ NH_3D + M = NH_2D + H + M \end{cases}$$

$$\text{II.}\ NH_3 + D_2 = NHD_2 + H_2 \qquad \text{IV.}\ \begin{cases} D_2 = D + D \\ NH_3 + D = NH_2D + H \\ H + D_2 = HD + D \end{cases}$$

The dissociation mechanism according to (I) cannot contribute very much to the exchange reaction for the following reason (cf. A. and L. Farkas, *Proc. Roy. Soc., loc. cit.*). The maximum speed of this mechanism is given by the number of collisions between D atoms and NH_2 radicals, which is several orders of magnitude smaller than the number of exchange processes actually observed, even if we make the very improbable assumption that the dissociation constant for ammonia is 20 times larger than that for deuterium.

In the molecular exchange mechanism (*II*), τ should be proportional to the reciprocal of the ammonia pressure, whereas the variation found is much less.

Mechanism (III) is suggested by L. Farkas and Harteck's investigation (*Z. physikal. Chem.*, 1934, *B*, **25**, 257) on the stationary hydrogen-atom concentration in the photo-decomposition of ammonia, in which they found evidence for a kinetic equilibrium $H + NH_3 \rightleftharpoons NH_4$. It is obvious that such a mechanism would lead to an exchange according to $D + NH_3 \rightleftharpoons NH_3D \rightleftharpoons NH_2D + H$, *provided the fourth hydrogen atom is bound* similarly to the other three. Further, they assume that association of $H + NH_3$ occurred at every ternary collision and required no activation energy.

Since it is now found that the apparent energy of activation is definitely larger than the energy necessary for the production of an atom by molecular dissociation, and the dependence of the reaction rate ou pressure is much less than one would expect for a reaction involving ternary collisions, it may be concluded that the formation and dissociation of the ammonium radical does not lead necessarily to an exchange of atoms. A possible explanation for this behaviour is that the fourth hydrogen atom is bound with much less energy (according to Farkas and Harteck, 10 kg.-cals.) than the other three, and in the dissociation act the bond with this fourth atom is broken (Taylor and Jungers, *J. Chem. Physics*, 1934, **2**, 452).

On the basis of previous experiments on the relatively high reactivity of free hydrogen atoms, it was expected that the mechanism (IV), involving the attack of a deuterium atom on an ammonia molecule, would be the most probable one, and actually this mechanism accounts satisfactorily, as will be seen, for the kinetics of the exchange reaction between ammonia and deuterium if one assumes that in this mechanism the rate-determining step is the reaction $D + NH_3 \rightleftharpoons NH_2D + H$, which proceeds about 30—40 times more slowly than the step $H + D_2 \rightleftharpoons HD + D$.

In order to deduce the kinetic equation of this exchange reaction, we must investigate the dissociation equilibria $NH_3 = NH_2 + H$ and $D_2 = D + D$, and then calculate the *stationary hydrogen- and deuterium-atom concentrations which* are established by the exchange reactions $D + NH_3 = NH_2D + H$, $H + D_2 = HD + D$, etc.

The dissociation equilibrium of D_2 is known and is given by the expression

$$\log K_{D_2} = \log \frac{P_D^2}{P_{D_2}} = -\frac{Q_0}{4{\cdot}57T} + \frac{3}{2}\log T + \frac{1}{4{\cdot}57}\int\frac{T}{T^2}\int C'_{D_2}\,dT + 2i_D - i_{D_2} \quad (12)$$

(Q_0 = energy of dissociation at absolute zero, C' = vibrational specific heat, i = chemical constant).

For the dissociation of NH_3 into NH_2 and H a similar expression is valid:

$$\log K_{NH_3} = \log \frac{P_H \cdot P_{NH_2}}{P_{NH_3}} = -\frac{Q_0}{4{\cdot}57T} + \frac{5}{2}\log T + \frac{1}{4{\cdot}57}\int\frac{dT}{T^2}\int C'_{NH_2}dT$$

$$-\frac{1}{4{\cdot}57}\int\frac{dT}{T^2}\int C'_{NH_3}\,dT + i_H + i_{NH_2} - i_{NH_3} \quad . \quad . \quad (13)$$

but we have far less information for this equilibrium than for the preceding one.

The term $\frac{5}{2}\log T$ is introduced in (13) instead of $\frac{3}{2}\log T$ since the molar heats of the polyatomic molecules NH_3 and NH_2 are:

$$C_{p,\,NH_3} = \tfrac{8}{2}R + C'_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14a)$$

and

$$C_{p,\,NH_2} = \tfrac{8}{2}R + C'_{NH_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14b)$$

where the vibrational specific heats C'_{NH_3} and C'_{NH_2} are given by

$$C' = \sum_i \phi\left(\frac{h\nu_i c}{kT}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

ϕ denoting Einstein's function, h Planck's constant, k Boltzmann's constant, c the velocity of light, and ν_i the vibrational frequencies of the molecule (in cm.$^{-1}$). For NH_3, the following frequencies have been used: 3336, 3300 (double), 1630 (double), and 950 cm.$^{-1}$; and for NH_2, in the absence of better values, those of the similarly shaped H_2O, *viz.*, 3895, 3803, and 1635 cm.$^{-1}$.

The chemical constants have the following values:

$$i_H = -1{\cdot}28 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16a)$$

$$i_{NH_2} - i_{NH_3} = \tfrac{3}{2}\log\frac{M_{NH_2}}{M_{NH_3}} + \log\frac{\bar{I}_{NH_2}}{\bar{I}_{NH_3}} + \log\frac{g_{NH_2}}{g_{NH_3}} \cdot \frac{s_{NH_3}}{s_{NH_2}} \quad . \quad . \quad (16b)$$

M denoting the mass, $\bar{I}$ the average moment of inertia ($\bar{I} = \sqrt{I_A I_B I_C}$), g the multiplicity, and s the symmetry number (3 for NH_3; 2 for NH_2).

The three moments of inertia for NH_3 are $I_A = I_B = 2{\cdot}8 \times 10^{-40}$ and $I_C = 4{\cdot}4 \times 10^{-40}$ g.-cm.^{2}. For NH_2 we obtain $I_A = 2{\cdot}7 \times 10^{-40}$, $I_B = 3{\cdot}0 \times 10^{-40}$, and $I_C = 0{\cdot}9 \times 10^{-40}$ g.-cm.^{2}, if we take the N–H and H–H distances and the angle between the two N–H bonds the same as in NH_3 (N–H = 1·02; H–H = 1·64 Å.).*

Assuming the ground state of NH_3 to be a singlet ($g_{NH_3} = 1$) and that of NH_2 a doublet ($g_{NH_2} = 2$), we obtain $i_H + i_{NH_2} - i_{NH_3} = 1{\cdot}1$.

The double integrals have the value of $-0{\cdot}18$ at the neighbourhood of $T = 1000°$ Abs., and we obtain for this temperature range

$$K_{NH_3} = -\frac{Q_0}{4{\cdot}57T} + \tfrac{5}{2}\log T - 1{\cdot}28 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Q_0 is not known accurately. An upper limit is given as 120 kg.-cals., since at a wavelength corresponding to this energy the spectrum of ammonia shows predissociation to $NH_3 = NH_2 + H$ (Bonhoeffer and Farkas, *Z. physikal. Chem.*, 1927, **139**, 337).

The average binding energy of the NH bond in ammonia is about 83 kg.-cals., but this does not necessarily imply that in the separation of the first hydrogen atom the same amount of energy is spent. It is more likely that the dissociation energy of this atom is

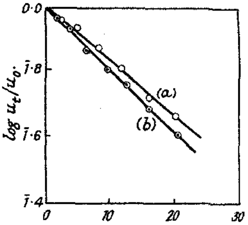
* The author has to thank Dr. Sutherland for the data concerning the NH_2 molecule.

much larger, for in water the dissociation energy for $H_2O = HO + H$ is 117 and that for $OH = O + H$ is 102 kg.-cals. (Bonhoeffer and Reichardt, *ibid.*, 1928, **139**, 75). Bonhoeffer and Harteck (" Grundlagen der Photochemie," Steinkopf, Dresden und Leipzig, 1933, p. 81) take the dissociation energy as 117 kg.-cals., which was deduced from the infra-red spectrum of ammonia by Ellis (*Physical Rev.*, 1929, **33**, 27). With this value we obtain at 1000° Abs., $\log K_{NH_3} = -25{\cdot}6 + 7{\cdot}5 - 1{\cdot}3 = -19{\cdot}4$, or $K_{NH_3} = 4 \times 10^{-20}$, whereas the dissociation constant for D_2 is $K_{D_2} = 3{\cdot}7 \times 10^{-18}$ (Johnston and Long, *J. Chem. Physics*, 1934, **2**, 389).

Naturally, the value for K_{NH_3} so obtained is very uncertain, owing mainly to the uncertainty in the value of Q_0; *e.g.*, if we assume $Q_0 = 108$ kg.-cals., we obtain the same dissociation constant for ammonia as for deuterium.

Attempts to obtain some information about the dissociation of ammonia experimentally were made as follows. The thermal reconversion of para-hydrogen is caused by the reaction $H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H$, and the reaction rate is governed by the hydrogen-atom concentration (A. Farkas, *Z. physikal. Chem.*, 1930, *B*, **10**, 419). If ammonia is dissociated, its presence should increase the reaction velocity in proportion to the additional atoms produced by its dissociation. It was found that the rate of reconversion of 16 mm. of *p*-hydrogen was only increased 1·15-fold when 251 mm. of ammonia were added (see Fig. 3, in which *u* denotes the excess concentration of $p\text{-}H_2$ relative to equilibrium). From this experiment, we can conclude that on addition of ammonia the hydrogen-atom concentration is scarcely altered, and we are justified in assuming that it is governed by the dissociation of hydrogen, whereas the dissociation of ammonia is negligible.

FIG. 3.



Time, minutes. 623°.
(*a*) *Without* NH_3 *addition.*
(*b*) *With* NH_3 *addition.*

We can now estimate the stationary H- and D-atom concentrations established in a mixture of deuterium and ammonia if the exchange reactions (18) and (19) occur.

$$H + D_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HD + D \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

$$D + NH_3 \underset{k_6}{\overset{k_5}{\rightleftharpoons}} NH_2D + H \quad . \; . \; . \; . \; . \; . \; . \; . \quad (19)$$

Naturally, as soon as some HD and NH_2D are formed, the reactions

$$H + HD \underset{k_4}{\overset{k_3}{\rightleftharpoons}} H_2 + D \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

$$D + NH_2D \underset{k_8}{\overset{k_7}{\rightleftharpoons}} NHD_2 + H \quad . \; . \; . \; . \; . \; . \; . \; . \quad (21)$$

followed by

$$D + NHD_2 \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} ND_3 + H \quad . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

come into play. For the sake of simplicity, we will assume that there are only two forward and two backward reactions :

$$H + (\text{heavy hydrogen}) \rightleftharpoons D + (\text{light hydrogen}) \quad . \; . \; . \; . \quad (23)$$

$$D + (\text{light ammonia}) \rightleftharpoons H + (\text{heavy ammonia}) \quad . \; . \; . \; . \quad (24)$$

where the names " light " and " heavy " designate the mixture of the corresponding compounds. If we assign to forward and reverse reactions the same velocity constants, we have

$$k_{\text{I}} = k_1 = k_4 = 2k_3 = 2k_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (25)$$

and

$$k_{\text{II}} = k_5 = k_{10} = \tfrac{3}{2}k_7 = \tfrac{3}{2}k_8 = 3k_9 + 3k_6{}^* \quad . \; . \; . \; . \quad (26)$$

* These two sets of velocity constants lead to the establishment of the equilibria (1), (2), (3), and (4).

Although from previous experiments we know that for the reactions (18) and (20) this is not exactly true, k_1/k_4 being $= 0{\cdot}48$, yet this simplification does not involve a great error in the calculation of the velocity constants, since that for the reactions (18) and (20) will turn out to be 30 times larger than that for the reactions (19), (21), and (22), and therefore the difference between the individual constants in one reaction might be neglected.

We will assume that at the beginning of the reaction a stationary H- and D-atom concentration is established which is invariant during the course of the reaction. Since the rate of the exchange reaction is much larger than the rate of dissociation and recombination of atoms, we might neglect the contribution of the last two processes to the alteration of the H- and D-atom concentration. The stationary concentration is reached if the production and consumption of H and D atoms by exchange is equal. If at the beginning of the reaction we start with 100% D_2 and pure NH_3 (pressures P_{D_2} and P_{NH_3}), then if the deuterium content of the hydrogen has decreased to u%, that of the ammonia has become $x = (1 - u)2P_{D_2}/3P_{NH_3}$. The numbers of hydrogen atoms produced and disappearing are given by (27) and (28) respectively :

$$[D]\{k_2[HD] + k_4[H_2] + k_5[NH_3] + k_7[NH_2D] + k_9[NHD_2]\} \quad . \quad . \quad (27)$$

$$[H]\{k_1[D_2] + k_3[HD] + k_6[NH_2D] + k_8[NHD_2] + k_{10}[ND_3]\} \quad . \quad . \quad (28)$$

For the stationary state these two expressions are equal.

If we introduce the simplification relating to the individual velocity constants, (25) and (26), and remember that as a consequence of (5)—(8)

$$[H_2] = (I - u)^2P_{D_2} \quad . \quad . \quad . \quad . \quad (29a) \qquad [NH_3] = (I - x)^3P_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad (30a)$$

$$[HD] = 2(1 - u)P_{D_2} \quad . \quad . \quad . \quad . \quad (29b) \qquad [NH_2D] = 3(1 - x)^2xP_{NH_3} \quad . \quad . \quad (30b)$$

$$[D_2] = u^2P_{D_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (29c) \qquad [NHD_2] = 3(1 - x)x^2P_{NH_3} \quad . \quad . \quad (30c)$$

$$[ND_2] = x^3P_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (30d)$$

and

$$x = (1 - u)2 \, . \, P_{D_2}/3P_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

we obtain, by equating (27) and (28), for the ratio $f = [H]/[D]$:

$$f = \frac{[H]}{[D]} = \frac{k_I P_{D_2} \, . \, (1 - u) + k_{II}P_{NH_3}(1 - x)}{k_I P_{D_2}u + k_{II}P_{NH_3}x} \quad . \quad . \quad . \quad . \quad . \quad (32)$$

or, introducing (31),

$$f = \frac{[H]}{[D]} = \frac{P_{D_2}(k_I - \frac{2}{3}k_{II})(1 - u) + k_{II}P_{NH_3}}{P_{D_2}(k_I - \frac{2}{3}k_{II})u + \frac{2}{3}k_{II}P_{D_2}} \quad . \quad . \quad . \quad . \quad . \quad (32a)$$

This ratio will define [H] and [D] during the reaction if we know either [H] or [D] or [H] + [D].

At the beginning of the reaction we have practically only deuterium atoms, their concentration being

$$[D]_0 = \sqrt{K_{D_2}P_{D_2}} \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

By the exchange reactions (23) and (24), hydrogen atoms are formed at the expense of these deuterium atoms. Since both types of atom disappear by forming H_2, D_2, and HD molecules

$$[D]_0 = [H] + [D] \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

if we assume that the recombination constants for H_2 and D_2 are equal and that for HD is twice as large.* The formulæ (32), (33), and (34) define [H] and [D] during the reaction.

Experimentally, the change in the deuterium content of the hydrogen (u) is measured, and this is governed by the equation

$$- du/dt = k_I\{[H]u - [D](1 - u)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

or, with $[H]/[D] = f$, as given by the equation (32a),

$$-\frac{du}{dt} = k_I[D]\left\{\frac{(k_{II}P_{NH_3} + \frac{2}{3}k_{II}P_{D_2})u - \frac{2}{3}k_{II}P_{D_2}}{P_{D_2}(k_I - \frac{2}{3}k_{II})u + \frac{2}{3}k_{II}P_{D_2}}\right\} \quad . \quad . \quad . \quad . \quad (36)$$

* This is not exactly true, and involves the same simplification as formula (25).

If we introduce, instead of u, the excess concentration relative to equilibrium [cf. (11)]

$$Z = u - P_{D_2}/(\tfrac{3}{2}P_{NH_3} + P_{D_2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

we obtain

$$-\frac{dZ}{dt} = \frac{k_I k_{II}[D](\frac{3}{2}P_{NH_3} + P_{D_2})Z}{\frac{3}{2}P_{D_2}[(k_I - \frac{2}{3}k_{II})u + \frac{2}{3}k_{II}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

or if we express [D] in terms of K_{D_2} and P_{D_2} according to equations (32), (33), and (34)

$$-\frac{dZ}{dt} = \frac{k_{II}(P_{NH_3} + \frac{2}{3}P_{D_2})\sqrt{K_{D_2}P_{D_2}}Z}{P_{D_2} + P_{NH_3}k_{II}/k_I} \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

This formula interprets the experimental data obtained for the reaction velocity (cf. $Z_t = Z_0 e^{-k^*t}$, p. 27) since

$$k^* = \frac{k_{II}(P_{NH_3} + \frac{2}{3}P_{D_2})\sqrt{P_{D_2}K_{D_2}}}{P_{D_2} + P_{NH_3}k_{II}/k_I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39a)$$

In order to find the values for k_I and k_{II}, it is the best to compare the velocity of the exchange reactions with that of the reaction $H_2 + D_2$ (cf. Table II), the rate of which is given by

$$dm/dt = 2k_1k_4\sqrt{K_{H_2}P_{H_2} + K_{D_2}P_{D_2}}\,m/(k_1 + k_4) \quad . \quad . \quad . \quad (40)$$

with $m = [HD]_\infty - [HD]$.
If we put $k_I = k_1 = k_4$, we have

$$dm/dt = k_I \times 1{\cdot}65\sqrt{K_{D_2}P_{D_2}}\,m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

since $P_{H_2} = P_{D_2}$ and $K_{D_2}/K_{H_2} = 1{\cdot}74$ at 1000° Abs.
If we put $P_{D_2} = P_{NH_3}$ in equation (39), we obtain

$$-dZ/dt = 1{\cdot}67Zk_Ik_{II}\sqrt{K_{D_2}P_{D_2}}/(k_I + k_{II}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

The relative rate of the reactions between H_2 and D_2 and between NH_3 and D_2 is given by $(k_I + k_{II})/k_{II}$, which is 30—40 according to col. 6 of Table II. From these values, we find for the ratio k_I/k_{II} the figures listed in col. 7 of Table II. According to these figures it seems that the ratio k_I/k_{II} increases with decreasing temperature. Such a behaviour is to be anticipated if the slowness of the reaction $D_2 + NH_3$ compared with the reaction $H_2 + D_2$ is due to a higher energy of activation.

We can compare the dependence of the reaction velocity on the ammonia and the deuterium pressure, as found experimentally (see p. 28) and as given by formula (39), in the following way. From the measurements of the interaction between H_2 and D_2, we find $k_I\sqrt{K_{D_2}} = 0{\cdot}070$ at 1000° Abs. and 0·0168 at 953° Abs. (pressure in mm. Hg; time in minutes). With the values $k_I/k_{II} = 35$ and 40, we obtain $k_{II}\sqrt{K_{D_2}} = 0{\cdot}00200$ and 0·00042 at these two temperatures respectively. Using these values, we can calculate k^* according to formula (39a) and compare the calculated figures with those obtained from the experimental half-life times (τ) according to $k^* = (\log_e 2)/\tau$. The calculated and observed values of k^* are listed in Table III. Evidently, the dependence of the reaction rate on both the ammonia and the deuterium pressure is represented fairly well by formula (39) in the pressure range investigated, and the agreement between theory and experiment is therefore satisfactory.

The next question to decide is why reaction (19) is so much slower than (18). The kinetic cross-sections of ammonia and hydrogen (or deuterium) are very nearly equal. The collision frequency between two particles with masses m_1 and m_2, being proportional to $\sqrt{(m_1 + m_2)/m_1m_2}$, will differ in these two reactions by the factor $\sqrt{[(2 + 17)/2 \times 17][4 \times 1/(4 + 1)]} = 0{\cdot}67$. If we allow for this difference in the collision frequencies, we still find that reaction (19) proceeds about 25 times more slowly than reaction (18). This lower reactivity can be due either to a lower steric factor or to a higher activation energy. The activation energy for the reaction $D + NH_3$ can be estimated in

TABLE III.

p_{D_2}.	p_{NH_3}.	k^* (obs.).	k^* (calc.).	p_{D_2}.	p_{NH_3}.	k^* (obs.).	k^* (calc.).
			Temperature 953° Abs.				
22	72	0·0080	0·0072	10	207	0·0153	0·0186
19	137	0·0119	0·0123	21	191	0·0182	0·0153
22	185	0·0144	0·0147	22	185	0·0144	0·0148
22	191	0·0181	0·0151	40	207	0·0147	0·0136
21	378	0·0209	0·0258	65	208	0·0154	0·0121
			Temperature 1000° Abs.				
16	20	0·0144	0·0148	16	114	0·0460	0·0515
15	54	0·0313	0·0302	17	95	0·0383	0·0442
20	76	0·0406	0·0360	31	106	0·0363	0·0377
17	95	0·0384	0·0445	40	86	0·0345	0·0336
16	114	0·0460	0·0515	107	105	0·0460	0·0329
14	177	0·0575	0·0730				
17	200	0·0638	0·0766				

two different ways: (i) from the apparent heat of activation calculated from the dependence of the reaction rate on temperatures; (ii) from the relative rate of the reactions (19) and (18). The apparent heat of activation is 62 kg.-cals., and contains also half of the dissociation energy of D_2 (52 kg.-cals.) which is used up in the formation of the D atoms. By subtracting this figure, we obtain 10 kg.-cals. as the energy of activation of the reaction (19). This value is definitely higher than the average activation energy of the reactions (18) and $D + H_2 = HD + H$, which is about 6 kg.-cals.

From the relative rate of 25, we can estimate the additional heat of activation if we assume that the steric factors for (19) and (18) are equal. From the formula $\log_e 25 = \Delta A/RT$, we find the additional energy of activation (ΔA) at 1000° Abs. to be 6·5 kg.-cals., giving 12·5 kg.-cals. as the total energy of activation for the reaction (19).

The discrepancy between the energy of activation as calculated from the dependence of the reaction velocity on temperature and from the relative rate disappears if we assume that the steric factor for the interchange between D and NH_3 is only 1/4 of that of the reaction $H_2 + D_2$, which is about 0·07 (Farkas and Farkas, *loc. cit.*).

One might be inclined to regard this smaller steric factor as due to the fact that in the pyramidal ammonia molecule the area of attack for the deuterium atom is restricted to the position of the nitrogen atom, whereas any approach of the deuterium to the hydrogen atoms cannot lead to an exchange reaction. On the other hand, in the deuterium molecule both atoms are equally reactive. Such a connexion is, however, purely qualitative, since it was shown by Wigner (*Z. physikal. Chem.*, 1932, *B*, **19**, 203) that in the interaction of hydrogen atoms and molecules only those atoms are exchanged which are coming from a certain direction (determined by a relatively small spatial angle relative to the molecular axis), and we do not know the magnitude of this angle determining the favourable directions for the interchange $D + NH_3$.

A definite evaluation of the energy of activation and steric factor involved in reaction (19) could be carried out by using a wider temperature range. Geib and Steacie (*ibid.*, 1935, *B*, **29**, 215) investigated this interaction at room temperatures, the deuterium atoms being produced in a discharge tube; they found that at 100° the velocity is only 6 times slower than the exchange reaction between hydrogen atoms and molecules investigated by Geib and Harteck (*ibid.*, Bodensteinband, 1931, p. 849) with the same technique. These results cannot be reconciled with those of the present investigation carried out at high temperatures, since even an additional activation energy of only 3 kg.-cals. should make the reaction $D + NH_3$ go 60 times more slowly at 100° than the reaction $H + H_2$.

To obtain some more information about the exchange reaction (19) at low temperatures, the mercury-sensitised photo-reaction was investigated, in which the hydrogen (or deuterium) atoms are formed by impact with excited mercury atoms. Preliminary experiments * have given the following results (room temperature; pressure 50—100 mm.): (1) The relative rates of the mercury-sensitised ortho-para conversion for H_2 and D_2 are in the ratio

* For details, see a forthcoming paper in collaboration with Melville.

ca. 1·4 : 1; this result is in agreement with the experiments of A. and L. Farkas on the thermal conversion of ortho-deuterium, and shows that the activation energy for the reaction $D + D_2 = D_2 + D$ is practically the same as that for $H + H_2 = H_2 + H$. (2) The rate of the para-hydrogen conversion remains unaltered if ammonia is added or if the short-wave range of the mercury light is cut out by an acetic acid filter. (3) In the unfiltered mercury light, an exchange reaction is observed between NH_3 and D_2 proceeding about 5 times more slowly than the conversion of para-hydrogen. (4) This exchange reaction is practically completely stopped if the short-wave range of the mercury radiation is cut out.

The last two results are in agreement with earlier experiments carried out by Taylor and Jungers (*loc. cit.*), according to which the exchange reaction can be accounted for by a decomposition of ammonia in the short-wave light and by a subsequent regeneration of the ammonia molecule from NH_2 and D. Comparison of the relative rates of the para-hydrogen conversion and of the exchange reaction reveals that the collision efficiency of reaction (19) is at least 100 times smaller at room temperature than the collision efficiency of the reaction $H + H_2 = H_2 + H$. Such a relative collision efficiency is compatible with the results of the present investigation, but is in marked disagreement with those of Geib and Steacie. Whether, and to what extent, the relatively high collision efficiency found by these authors is due to processes other than the interaction of $D + NH_3$ in the gas phase, requires further investigation.

Finally, it is recorded that, including some preliminary experiments with methane and water at 1000° Abs., the following relative rates were found for the given exchange reactions:

$D_2 + H_2$	:	$D_2 + CH_4$	:	$D_2 + NH_3$	:	$D_2 + H_2O$
100	:	20	:	3	:	1

This series does not agree with the experiments of Geib and Steacie by the atomic hydrogen technique at and above room temperature, since these authors find that the exchange reaction with methane is the slowest. No explanation can yet be given for this discrepancy, but the possibility of wall reactions cannot be ignored.

Summary.

The kinetics of the exchange reaction between ammonia and deuterium have been investigated in the gas phase at 680—780° and at pressures of 10—400 mm. of mercury.

The progress of the reaction, the dependence of its rate on the partial pressures and on temperature, and its absolute rate can be satisfactorily explained by assuming that the rate-determining step $D + NH_3 = NH_2D + H$ occurs 30—40 times more slowly than the reaction $H + D_2 = HD + D$.

The atoms responsible for the exchange reaction are formed by the thermal dissociation of deuterium, that of ammonia ($NH_3 = NH_2 + H$) being negligible. The lower reactivity of deuterium atoms with ammonia than of hydrogen with deuterium is due to the fact that the energy of activation for the former reaction is 11 ± 1 kg.-cals., and may be partly due to a lower steric factor. This result is in agreement with some preliminary experiments on the mercury-sensitised photochemical exchange reaction between D and NH_3.

The author has great pleasure in expressing his indebtedness to Professor E. K. Rideal, F.R.S., for his constant interest in this work, for many helpful discussions, and for the hospitality of his laboratory. He is also indebted for financial assistance to the Central British Fund for German Jewry and to the Imperial Chemical Industries Ltd.

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7. *The Parachor, Surface Tension, and Density of Substituted Phenols and Phenolic Ethers.*

By A. BURAWOY and I. MARKOWITSCH-BURAWOY.

IN continuation of previous work on the constitution of the so-called *o*-hydroxyazobenzenes (*o*-benzoquinonephenylhydrazones; Burawoy and Markowitsch, *Annalen*, 1933, **503**, 180; **504**, 71; 1934, **509**, 60; 1935, in the press), the parachors, surface tensions, and densities of the hydroxyazobenzenes and hydroxybenzaldehydes and their methyl ethers have been investigated, and are discussed in relation to the same properties of the nitrophenols and -anisoles (given by, or calculated from, Jaeger, *Z. anorg. Chem.*, 1917, **101**, 1).

The theoretical parachors were calculated from Sugden's atomic values (" The Parachor and Valency "). The outstanding feature of the results (Table I) is the low value of the parachor of *o*-hydroxy-compounds in comparison, not only with theoretical values, but also with those of corresponding *m*- or *p*-hydroxy-compounds, whereas the methyl ethers in each series do not show these differences. That this negative anomaly cannot be attributed to association due to hydroxyl or amino-groups (Sugden, *op. cit.*) follows from the normal values afforded by (7) and (17) (cf. also Sidgwick and Bayliss, J., **1930**, 2027).

The calculated parachors of *o*-hydroxyazo-compounds are identical with those of the corresponding quinonephenylhydrazones, and so determinations cannot decide between the two structures.

TABLE I.

	Substance.	Parachor. Obs.	Calc.	Diff.	γ	*D.*	
1	Benzeneazo-β-naphthol methyl ether	594·4	593·1	+ 1·3	40·6	1·113	At 100°
2	β-Naphthaquinone-α-phenylhydrazone	545·8	554·1	− 8·3	40·7*	1·154*	
3	*o*-Methoxyazobenzene	486·9	487·2	− 0·3	36·7	1·073	
4	*m*- ,,	486·9	487·2	− 0·3	35·6	1·062	
5	*p*- ,,	485·0	487·2	− 2·2	36·2	1·071	
6	*o*-Benzoquinonephenylhydrazone	443·3	448·2	− 4·9	35·8	1·094	
7	*m*-Hydroxyazobenzene	449·8	448·2	+ 1·6	42·5*	1·123*	
8†	*p*- ,,	—	—	—	41·6*	—	
9	*o*-Nitroanisole	320·5	323·1	− 2·6	39·5	1·197	At 75°
10‡	*p*- ,,	322·0	323·1	− 1·1	39·9	1·201	
11‡	*o*-Nitrophenol	270·3	284·1	− 13·8	36·1	1·258	
	,,	—	—	—	31·1	1·205	At 125°
12‡	*m*- ,,	278·1	284·1	− 6·0	39·5	1·259	
13‡	*p*- ,,	280·9	284·1	− 3·2	42·5	1·266	
14‡	*o*-Methoxybenzaldehyde	309·9	314·1	− 4·2	37·1	1·083	At 75°
15	*p*- ,, ,,	310·2	314·1	− 3·9	36·4	1·077	
16‡	*o*-Hydroxybenzaldehyde	271·3	275·1	− 3·8	36·7	1·104	
17	*p*- ,, ,,	276·5	275·1	+ 1·4	47·8*	1·173*	

† See p. 39. ‡ Values of γ and D are due to Jaeger (*loc. cit.*).

The density, and much more so, the surface tension, is even more significant than the parachor. The values for any one series are always compared at the same temperature; although this is arbitrarily chosen, the same conclusions could be derived by adoption of any other temperature. For convenience the values of some substances (denoted by *) are extrapolated and given for a temperature at which they are in fact solid.

According to Table I, the surface tensions and the densities of the three sets of isomeric methyl ethers agree among themselves within 2%, but in the corresponding hydroxy-compounds the *o*- has a lower surface tension (by 20—35%) and density (by 3—6%) than its isomerides. This anomaly is also apparent in that, in the *m*- and *p*-series, the methyl ethers always have much smaller surface tensions (by 20—30%) than their phenols, as normally all hydroxylic compounds and their methyl ethers behave, whereas in the *o*-series the difference is slightly in the other direction.

It is known (v. Auwers and co-workers, *Z. physikal. Chem.*, 1895, **18**, 595; 1897, **21**, 335; 1899, **30**, 300; 1903, **42**, 513) that *m*- and *p*-hydroxybenzaldehydes, -nitrophenols,

and -hydroxyazobenzenes are extensively associated in several solvents, but the *o*-derivatives are only slightly associated. Evidence for the behaviour in the homogeneous fused state could be derived from the Ramsay–Shields constant K (J., 1893, **63**, 1089), which is usually 2·12 for non-associated compounds. In Table II are given the calculated values, together with the derived association factor x, although these are now known to have only qualitative, and not quantitative, significance. The values of the nitroanisoles and of *o*-nitrophenol indicate no association, but those of *p*- and still more so of *m*-nitrophenol indicate considerable association (compare Hewitt and Winmill, J., 1907, **91**, 441). Similarly, *o*- and *p*-methoxy- and *o*-hydroxy-benzaldehyde are normal, but *p*-hydroxybenzaldehyde is associated. On the other hand, all methyl ethers of the hydroxyazo-

TABLE II.

Substance.	Temp. range.	K.	x.	Substance.	Temp. range.	K.	x.
Benzeneazo-β-naphthol methyl ether	83—114°	3·1	0·57	*o*-Nitroanisole	55—95°	2·2	0·95
o-Methoxyazobenzene	56·5—88·5	2·8	0·66	*p*- ,, ...	115—167·5	2·2	0·95
m- ,, ,,	53—81·5	2·9	0·63	*o*-Nitrophenol...........	124·3—170	2·5	0·77
p- ,, ,,	67—98	2·9	0·63	*m*- ,, ...	125—170	1·0	3·08
o-Benzoquinonephenylhydrazone	100—130	2·4	0·83	*p*- ,, ...	130·5—176·5	1·7	1·39
m-Hydroxyazobenzene	120—148	2·5	0·77	*o*-Methoxybenzaldehyde	52—91	2·3	0·89
β-Naphthaquinone-α-phenylhydrazone ...	150·5—188	2·6	0·74	*p*- ,, ,,	46·5—90·3	2·2	0·95
				o-Hydroxybenzaldehyde	116·2—160	2·0	1·09
				p- ,, ,,	117—145	1·6	1·53

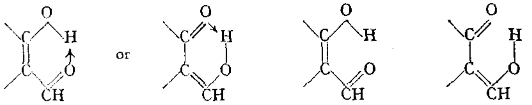
benzenes have $x < 1$, implying that in this case the normal value of K is not 2·12, so the lower K values of the two phenylhydrazones may indicate a small association; however, *m*-hydroxyazobenzene gives a similar value for K, although a higher association would be expected. (Possibly comparison of the last two types of compound is invalidated by structural differences.) Hence, von Auwers's results appear to be confirmed for the fused nitrophenols and hydroxybenzaldehydes, but the behaviour of the hydroxyazobenzenes is not clear.

Steric hindrance cannot be the cause of the anomalies in the *o*-hydroxy-compounds, for the densities, surface tensions, and parachors of the methoxy-compounds are normal, although they might be expected to exhibit equal or greater steric hindrance (compare also Sidgwick and Callow, J., 1924, **125**, 527 and previous papers). Moreover, the anomaly cannot be attributed to difference in atomic structure, for the absorption spectra (200—800 mμ) of the *o*-hydroxy- and -methoxy-benzaldehydes are very similar (Tuck, J., 1909, **95**, 1813; Waliaschko, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 754, 785); the spectra of *o*-nitrophenol and its methyl ether show larger differences, but their type is not changed (Baly, Edwards, and Stewart, J., 1906, **89**, 518; Waliaschko, *loc. cit.*, p. 1008). *o*-Nitrophenol and *o*-hydroxybenzaldehyde are therefore undoubtedly phenolic in structure; but the spectra of *o*-hydroxyazobenzenes show that they are actually quinonehydrazones (compare Burawoy and Markowitsch, *loc. cit.*).

The view that these anomalies are connected with a weakening of the polarity of the *o*-substituted phenols produced by interaction between the two *o*-substituents, similar to the formation of molecular compounds between phenols or anilines and nitrobenzenes, quinones, etc. (Sidgwick, *loc. cit.*), is confirmed by the anomalies of the surface tension, in which replacement of a CH by a CMe group has no appreciable effect on the value of the surface tension, but replacement of an OH by an OMe group generally produces a big decrease of the value. This is, undoubtedly, due to the association of the hydroxyl compounds. Therefore, *o*-substituted phenols, having lost the capacity to associate with other molecules, behave " normally " and have the same surface tension as their methyl ethers.

The anomalies of " *o*-hydroxyazobenzenes " may not necessarily be due to their quinonoid structure; for phenolic *o*-nitrophenol and *o*-hydroxybenzaldehyde show the same behaviour. Effects caused by intramolecular association between the two *o*-substituents would operate also in the alternative quinonehydrazone structure. It is known that the amino-group may replace a hydroxyl group in such compounds (compare Sidgwick, *loc. cit.*).

The association may be due to the formation of a new co-ordinate bond of the hydrogen atom (I) (Sidgwick) or to a dipole attraction between the associated groups (Smyth, *J. Amer. Chem. Soc.*, 1929, **51**, 1736; "Dielectric Constant and Molecular Structure," New York, 1931; Martin and co-workers, J., 1932, 2658; **1933**, 1413; *Trans. Faraday Soc.*, 1934, **30**, 759). However, strong evidence can be derived from the absorption spectra (λ 200—800 mμ) of the substituted phenols against the assumption that the constitution of the *o*-substituted phenols corresponds to an intermediate state between (II) and (III), possibly representing a very rapid oscillation between these two extreme states (Sidgwick, *Ann. Reports*, 1934, **31**, 37); *for the spectra of o-hydroxy- and o-methoxy-benzaldehyde*



(I.) (II.) (III.)

are almost identical, and that of β-benzeneazo-α-naphthol is completely different from that of its *O*-methyl ether, but similar to that of its *N*-phenyl ether (β-naphthaquinone-β-diphenylhydrazone). This evidence seems to exclude the assumption of such an intermediate state, which would certainly have an electron configuration (responsible for the absorption between 200 and 800 mμ) different from both the phenolic and the quinonoid structure.

Experimental.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27); r_2 for the bubbler used was 0·199 cm., and values of *A* are given for each set of determinations. Densities (*D*; g./c.c.) were determined with a U-shaped pyknometer (Sugden, J., 1924, **125**, 1171). For all the substances concerned, *d* is very small and has been neglected.

Benzeneazo-β-naphthol methyl ether (M = 262·1) was prepared according to Charrier and Ferreri (*Gazzetta*, 1912, **42**, 117) and recrystallised from alcohol; m. p. 62°. Densities determined: $D_{4°}^{84°}$ 1·1255; $D_{4°}^{93·5°}$ 1·1185; $D_{4°}^{104°}$ 1·1095; $D_{4°}^{115°}$ 1·1015. A = 0·004.

t.	*P*.	*D*.	*ϕ*.*	*γ*.	[*P*].	*t*.	*P*.	*D*.	*ϕ*.*	*γ*.	[*P*].
83·0°	10425	1·126	1·0146	42·30	593·6	104·0°	9909	1·110	1·0151	40·23	594·8
94·0	10148	1·118	1·0148	41·20	594·1	114·0	9645	1·102	1·0154	39·17	595·0
										Mean	594·4

* A correction factor; see Sugden, J., 1924, **125**, 31.

β-Naphthaquinone-α-phenylhydrazone (M = 248·1) was recrystallised from alcohol; m. p. 134°. Densities determined: $D_{4°}^{150·5°}$ 1·119; $D_{4°}^{160·5°}$ 1·112; $D_{4°}^{170·0°}$ 1·1055; $D_{4°}^{188°}$ 1·093. A ≈ 0·004.

150·0°	9003	1·119	1·0168	36·60	545·5	172·0°	8527	1·107	1·0175	34·68	545·5
160·5	8843	1·112	1·0169	35·93	546·5	188·0	8208	1·093	1·0179	33·41	545·8
										Mean	545·8

o-Methoxyazobenzene (M = 212·1) (Bamberger, *Ber.*, 1900, **33**, 3190) was recrystallised from ligroin; m. p. 41°. Densities determined: $D_{4°}^{55·5°}$ 1·107; $D_{4°}^{65·5°}$ 1·0985; $D_{4°}^{75·5°}$ 1·0915; $D_{4°}^{85·5°}$ 1·084 (v. Auwers and Hemke, *Ber.*, 1928, **61**, 1030, found $D_{4°}^{100°}$ 1·0728). A = 0·00391.

56·5°	10450	1·106	1·0143	41·43	486·7	75·5°	9937	1·092	1·0148	39·42	486·9
65·0	10248	1·099	1·0145	40·64	487·1	85·5	9657	1·084	10·151	38·32	486·9
										Mean	486·9

m-Methoxyazobenzene was prepared according to Jacobson and Hoenigsberger (*Ber.*, 1903, **36**, 4102) and recrystallised from ligroin; m. p. 33—34°. Densities determined: $D_{4°}^{53°}$ 1·1023; $D_{4°}^{62°}$ 1·0945; $D_{4°}^{73°}$ 1·086; $D_{4°}^{81·5°}$ 1·078. A = 0·005729.

53·0°	6970	1·1023	1·0213	40·78	486·2	73·0°	6595	1·0860	1·0222	38·61	486·8
62·0	6830	1·0945	1·0216	39·96	487·2	81·5	6443	1·0780	1·0225	37·75	487·4
										Mean	486·9

p-Methoxyazobenzene was recrystallised from alcohol; m. p. 56°. Densities determined : $D_{4°}^{67°}$ 1·097; $D_{4°}^{78°}$ 1·089; $D_{4°}^{88°}$ 1·0805; $D_{4°}^{98°}$ 1·073. A = 0·005729.

67·0°	6773	1·099	1·0219	39·65	484·4	88·0°	6352	1·081	1·0229	37·23	484·9
78·0	6568	1·089	1·0223	38·46	485·1	98·0	6210	1·073	1·0236	36·41	485·6
										Mean	485·0

m-Hydroxyazobenzene (M = 198·1) (Jacobson and Hoenigsberger, *Ber.*, 1903, **36**, 4102) was recrystallised from ligroin; m. p. 114—116°. Densities determined : $D_{4°}^{120°}$ 1·107; $D_{4°}^{130°}$ 1·099; $D_{4°}^{139°}$ 1·092; $D_{4°}^{148°}$ 1·084. A = 0·005729.

120·0°	6822	1·107	1·0219	39·93	449·1	139·0°	6436	1·092	1·0229	37·71	449·7
130·0	6592	1·099	1·0225	38·61	449·4	148·0	6346	1·084	1·0230	37·19	451·2
										Mean	449·8

p-Hydroxyazobenzene was recrystallised from alcohol; m. p. 154°. A determination of the density was not possible owing to decomposition above the m. p. The determination of the surface tension was carried out as quickly as possible after melting. The correction factor ϕ is calculated by assuming a density equal to that of *m*-hydroxyazobenzene. A = 0·00391.

176·0°	*8552*	*1·061*	*1·0167*	*34·00*	—	*165·0°*	*8326*	*1·052*	*1·0170*	*33·10*	—

o-Benzoquinonephenylhydrazone (M = 198·1) (Bamberger, *Ber.*, 1900, **33**, 3191) was recrystallised from ligroin; m. p. 83°. Densities determined : $D_{4°}^{100°}$ 1·094; $D_{4°}^{110°}$ 1·087; $D_{4°}^{120°}$ 1·078; $D_{4°}^{130°}$ 1·0705. A = 0·005729.

100·0°	6102	1·094	1·0242	35·79	442·9	120·0°	5814	1·078	1·0250	34·14	444·0
110·0	5923	1·087	1·0247	34·76	442·6	130·0	5625	1·0705	1·0256	33·05	443·7
										Mean	443·3

o-Methoxybenzaldehyde (M = 136·05) was purchased, distilled in a vacuum, and purified according to Katschalowsky and v. Kostanecki (*Ber.*, 1904, **37**, 2347); m. p. 39°. Densities determined : $D_{4°}^{51°}$ 1·104; $D_{4°}^{72°}$ 1·086; $D_{4°}^{81°}$ 1·078; $D_{4°}^{91°}$ 1·069 [v. Auwers (*Annalen*, 1915, **408**, 239) found $D_{4°}^{20·2°}$ 1·1326; Perkin (J., 1896, **69**, 1200) $D_{4°}^{4°}$ 1·1445; and Sidgwick and Bayliss (*loc. cit.*) $D_{4°}^{50·8°}$ 1·0992]. A = 0·005729.

52·0°	6763	1·103	1·0220	39·59	309·4	81·0°	6209	1·078	1·0234	36·39	310·1
72·0	6380	1·086	1·0229	37·38	309·8	91·0	6015	1·069	1·0240	35·28	310·1
										Mean	309·9

p-Hydroxybenzaldehyde (M = 122·05) was recrystallised from water; m. p. 115°. Densities determined : $D_{4°}^{117°}$ 1·143; $D_{4°}^{127°}$ 1·136; $D_{4°}^{135°}$ 1·129; $D_{4°}^{145°}$ 1·120 (Sidgwick and Bayliss found $D_{4°}^{119·6°}$ 1·1364; $D_{4°}^{136·7°}$ 1·1238). A = 0·005729.

117·0°	7600	1·143	1·0203	44·42	275·6	135·0°	7372	1·129	1·0206	43·05	277·1
127·0	7477	1·136	1·0205	43·71	276·3	145·0	7157	1·120	1·0211	41·90	277·2
										Mean	276·6

o-Nitroanisole (M = 153·06), a commercial specimen, after distillation in a vacuum, melted at 9°. Densities determined by Jaeger : $D_{4°}^{25°}$ 1·2472; $D_{4°}^{50°}$ 1·2218; $D_{4°}^{75°}$ 1·1970. The parachors calculated from Jaeger's values of density and surface tension are not concordant (variation 319·5—332·5) and are much too high (Calc. : 323·1). The densities determined by Schmidt (*Z. physikal. Chem.*, 1907, **58**, 525; $D_{4°}^{20°}$ 1·2540) and by Sidgwick and Bayliss ($D_{4°}^{25°}$ 1·2408, $D_{4°}^{57·4°}$ 1·2075) are in agreement with Jaeger's values. Sidgwick and Bayliss found $\gamma^{25°}$ 45·9, $\gamma^{57·4°}$ 42·3 (contrast Jaeger's values); these were confirmed in the present work. A = 0·005729.

26·0°	7809	1·2465	1·0215	45·70	319·4	77·0°	6698	1·195	1·0240	39·28	320·7
55·0	7155	1·217	1·0229	41·93	320·1	95·0	6400	1·177	1·0248	37·58	321·9
										Mean	320·5

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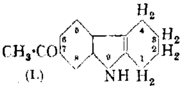
8. *Tetrahydrocarbazoles with Substituents in the 7-Position.*

By S. G. P. Plant and (Miss) K. M. Rogers.

Considerable uncertainty attaches to the structure assigned to several tetrahydrocarbazole derivatives with substituents in the 5- or the 7-position (numbering as in I), mainly through the failure of Fischer's indole synthesis to give unambiguous results when applied to *m*-substituted phenylhydrazones of *cyclo*hexanone (see, *e.g.*, J., 1921, **119**, 1825; 1923, **123**, 2393; 1926, 808, 2260; 1928, 2454). A recent investigation of the course of the Friedel–Crafts reaction in the carbazole series (Plant, Rogers, and Williams, J., 1935, 741) indicated that ketones with the side chain in the 7-position, which might be used in elucidating the structure of some of the above derivatives, might result from the action of acid chlorides on the 9-acyltetrahydrocarbazoles, and this has been shown to be the case. The 7-*acetyl* derivatives of 9-acetyl- and 9-benzoyl-tetrahydrocarbazole have been obtained by the use of acetyl bromide and aluminium chloride, and the constitution of the 7-*acetyltetrahydrocarbazole* (I) derived from them by hydrolysis has been established by oxidation with sulphur to 2-acetylcarbazole (D.R.-P. 555,312; *Chem. Zentr.*, 1932, ii, 2532; Plant and Williams, J., 1934, 1142). Owing to the difficulty of effecting complete purification of the 2-acetylcarbazole prepared by this process, confirmation of the structure was obtained by reducing (I) to 7-*ethylhexahydrocarbazole*, which was satisfactorily oxidised to 2-ethylcarbazole (Plant and Williams, *loc. cit.*). The 7-*benzoyl* derivatives of the two 9-acyltetrahydrocarbazoles have been similarly prepared by the use of benzoyl chloride and hydrolysed to 7-*benzoyltetrahydrocarbazole*, which has been oxidised to 2-benzoylcarbazole, the identity of the latter being confirmed by conversion into its 9-acetyl derivative (Plant, Rogers, and Williams, *loc. cit.*). The observation has also been made that, although 3-acetylcarbazole can readily be obtained by the action of aluminium chloride on 9-acetylcarbazole in nitrobenzene, 9-acetyltetrahydrocarbazole gives under similar conditions an unsatisfactory product from which a small amount of 7-acetyltetrahydrocarbazole can be isolated.



(I.)

Experimental.

7-Acetyltetrahydrocarbazole.—(a) A mixture of 9-acetyltetrahydrocarbazole (5 g., prepared from tetrahydrocarbazole and acetic anhydride as described by Perkin and Plant, J., 1921, **119**, 1832), carbon disulphide (50 c.c.), acetyl bromide (8 g.), and aluminium chloride (10 g.) was refluxed for 2½ hours, and the solvent allowed to evaporate. When the residue was scraped on to ice–dilute hydrochloric acid, 7 : 9-*diacetyltetrahydrocarbazole*, pale yellow prisms, m. p. 110°, from alcohol, was obtained (Found: C, 75·5; H, 6·6. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7%). Hydrolysis of the latter was effected by refluxing with aqueous-alcoholic potassium hydroxide for ½ hour, and 7-*acetyltetrahydrocarbazole*, pale yellow prisms, m. p. 206—208°, from alcohol, was precipitated by the addition of water (Found: C, 78·9; H, 7·1. $C_{14}H_{15}ON$ requires C, 78·9; H, 7·0%).

(b) Prepared similarly from 9-benzoyltetrahydrocarbazole (Perkin and Plant, J., 1923, **123**, 676), 9-*benzoyl-7-acetyltetrahydrocarbazole* separated from alcohol in colourless plates, m. p. 149° (Found: C, 79·4; H, 6·0. $C_{21}H_{19}O_2N$ requires C, 79·5; H, 6·0%), and gave 7-acetyltetrahydrocarbazole, identical with the above product (mixed m. p.), on hydrolysis.

(c) A solution of 9-acetyltetrahydrocarbazole (3·5 g.) in nitrobenzene (30 c.c.) was treated with aluminium chloride (2·5 g.) and kept at 120—125° for 15 minutes. The cooled solution was poured into dilute hydrochloric acid, the nitrobenzene removed in steam, and the residual solid boiled in alcohol with charcoal. When the product obtained by adding dilute hydrochloric acid to the filtered solution was distilled under reduced pressure and crystallised from acetic acid and then alcohol, a small quantity (about 0·2 g.) of 7-acetyltetrahydrocarbazole (mixed m. p.) was isolated.

A solution of the latter substance (4·1 g.) and sulphur (1·25 g.) in quinoline (50 c.c.) was boiled for an hour and poured into ice–dilute hydrochloric acid, and the product extracted with ether. The dried extract was evaporated, and the residue distilled, with the addition of iron filings, under reduced pressure. After the distillate had been crystallised twice from toluene

and then twice from acetic acid, 2-acetylcarbazole was obtained in colourless plates, m. p. 225° (after softening at 218°), and identified by mixed m. p. with an authentic specimen, m. p. 227°.

7-Acetyltetrahydrocarbazole (5·4 g.) was shaken with amalgamated granulated zinc (400 g.) and concentrated hydrochloric acid (100 c.c.), and left for several hours. After the addition of anisole (10 c.c.) and more hydrochloric acid (30 c.c.), the whole was refluxed for 12 hours, and the product extracted with ether. The extract was washed with water and evaporated, and anisole removed from the residue by distillation in steam. The less volatile product was again collected in ether and *7-ethylhexahydrocarbazole*, m. p. 44—46°, was extracted with dilute sulphuric acid; it was recovered by the addition of sodium hydroxide and purified by distillation under reduced pressure (Found: C, 83·9; H, 9·5. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5%). When this base was oxidised with sulphur in boiling quinoline as described above, and the product distilled with iron filings under reduced pressure, 2-ethylcarbazole, yellow plates, m. p. 223° (after two crystallisations from acetic acid), was obtained and identified by a mixed m. p. with an authentic specimen.

7-Benzoyltetrahydrocarbazole.—A mixture of 9-acetyltetrahydrocarbazole (5 g.), carbon disulphide (35 c.c.), benzoyl chloride (10 g.), and aluminium chloride (10 g.) was refluxed for 4 hours, most of the solvent allowed to evaporate, and the residue poured on ice–dilute hydrochloric acid. The more volatile material was removed in steam and the solid residue was collected, washed free from benzoic acid with aqueous sodium carbonate, and crystallised from alcohol and then acetic acid; *7-benzoyl-9-acetyltetrahydrocarbazole* was obtained in yellow plates, m. p. 126° (Found: C, 78·8; H, 5·9%). Prepared similarly from 9-benzoyltetrahydrocarbazole, 7 : *9-dibenzoyltetrahydrocarbazole* separated from glacial acetic acid in almost colourless prisms, m. p. 121° (Found: C, 81·8; H, 5·6. $C_{26}H_{21}O_2N$ requires C, 82·3; H, 5·5%). Both these compounds gave *7-benzoyltetrahydrocarbazole*, yellow needles, m. p. 165°, from glacial acetic acid, on hydrolysis with alkali as above (Found: C, 82·9; H, 6·3. $C_{19}H_{17}ON$ requires C, 82·9; H, 6·2%). This substance was oxidised with sulphur in quinoline, and the product distilled with iron filings under 0·7 mm. pressure. When the distillate was crystallised from acetic acid, it gave 2-benzoylcarbazole, m. p. 153°, after softening from 143°, which was purified by conversion into 2-benzoyl-9-acetylcarbazole by refluxing with acetic anhydride and a drop of sulphuric acid for 2 hours. The product obtained by precipitation with water then separated from alcohol in brown needles, m. p. 137°, and was identified by mixed m. p.

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9. *Researches on Residual Affinity and Co-ordination. Part XXXVI. The Constitution of "Ruthenium Red."*

By Gilbert T. Morgan and Francis H. Burstall.

In the course of his researches on ruthenium, Joly (*Compt. rend.*, 1892, **114**, 291; **115**, 1299) observed that the metal readily furnished ruthenium trichloride, $RuCl_3$, when heated at 360—440° in chlorine containing a little carbon monoxide. The dark brown chloride was stated to absorb ammonia with the formation of an ammine, $Ru_2Cl_6,7NH_3$. This partly dissolved in water, forming an intense violet-red solution from which a crystalline hydroxy-compound, $Ru_2Cl_4(OH)_2,7NH_3,3H_2O$, was obtained. The hydroxy-compound, also obtained by the action of ruthenium chloride on aqueous ammonia, is known as "ruthenium red" and dyes animal fibres in red shades. Joly (*loc. cit.*) also stated that "ruthenium red" gave the compound $Ru_2Cl_6(OH)_2,7NH_3,HCl,3H_2O$ on treatment with concentrated hydrochloric acid.

These results clearly require revision in the light of modern ideas on molecular constitution. Moreover, analyses were recorded only for the ammine $Ru_2Cl_6,7NH_3$, the corresponding bromide and iodide of which have been reported by Gutbier and Trenker (*Z. anorg. Chem.*, 1905, **45**, 166).

The action of chlorine containing a little carbon monoxide on ruthenium at temperatures between 380° and 420° gives a product consisting mainly of ruthenium trichloride. The preparations always contain traces of unchanged ruthenium and probably ruthenium dichloride (compare Howe, Howe, and Ogburn, *J. Amer. Chem. Soc.*, 1924, **46**, 335). The foregoing specimens of ruthenium trichloride absorb ammonia, but the product is a mixture

of amminated chlorides, probably including the hexammine chloride, $[Ru(NH_3)_6]Cl_3$, corresponding with the analogous ferric chloride derivative, $[Fe(NH_3)_6]Cl_3$ (Hüttig, *Z. anorg. Chem.*, 1920, **114**, 169; Ephraim and Millmann, *Ber.*, 1917, **50**, 531; Biltz and Birk, *Z. angew. Chem.*, 1924, **134**, 131). The mixture partly dissolves in water, giving the characteristic purple-red solution of "ruthenium red," which, however, is best prepared by the action of ruthenium trichloride on concentrated aqueous ammonia. It has now been found that "ruthenium red" is *chlorotetramminohydroxoruthenium chloride hydrate* (I), and this structure is supported by the derivatives shown in the following diagram:

$[RuCl_2(NH_3)_4]Cl,2H_2O$ (II.) $\rightleftharpoons$ $[Ru(OH)Cl(NH_3)_4]Cl,H_2O$ (I.) Ruthenium red. $\longrightarrow$ $[RuCl(NO_3)(NH_3)_4]NO_3,4H_2O$ (III.)

$[Ru(OH)Br(NH_3)_4]Br,H_2O$ (IV.) $\quad$ $[Ru(OH)Cl(NH_3)_4]I$ (VI.) $\quad$ $[Ru(OH)Cl(NH_3)_4]_2Ru(NO)Cl_5$ (IX.)

HBr $\downarrow \uparrow$ NH_3 $\qquad\qquad \downarrow$

$[RuBr_2(NH_3)_4]Br,H_2O$ (V.) $\quad$ $[Ru(OH)I(NH_3)_4]I$ (VII.) $\rightleftharpoons$ $[RuI_2(NH_3)_4]I$ (VIII.)

"Ruthenium red" (I) and hydrochloric acid give *dichlorotetramminoruthenium chloride dihydrate* (II), whereas nitric acid furnishes *chloronitratotetramminoruthenium nitrate tetrahydrate* (III), which does not react with silver nitrate except on warming. Aqueous potassium bromide and hydrobromic acid furnish (IV) and (V) respectively with "ruthenium red," and potassium iodide gives successively (VI) and (VII), the latter compound giving (VIII) with hydriodic acid. With potassium nitrosoruthenichloride, "ruthenium red" furnishes the sparingly soluble complex *salt* (IX).

The foregoing results provide strong evidence for the constitutional formula (I) for "ruthenium red," but further confirmatory results have been obtained by the isolation of analogues of this amminated ruthenium halide in which the ammonia molecules are replaced by ethylenediamine, ethylamine, and pyridine respectively.

Ethylenediamine Analogue of Ruthenium Red.—Aqueous ethylenediamine (en) reacts with ruthenium trichloride, forming a deep yellow solution from which alcohol precipitates *chlorobisethylenediaminohydroxoruthenium chloride* (X) in small yield. This compound

$$[RuCl_2en_2]Cl \ (XI.) \longleftarrow [Ru(OH)Cl\,en_2]Cl \ (X.) \longrightarrow [Ru(OH)I\,en_2]I \ (XII.)$$

does not possess the intense colour of the ammonia derivative, and reacts with hydrochloric acid, giving (XI), and with warm concentrated potassium iodide, precipitating (XII).

Pyridine Analogue of Ruthenium Red.—Aqueous pyridine and ruthenium trichloride combine very slowly at 90°, leading to *chlorotetrapyridinohydroxoruthenium chloride* (XIII), a yellow crystalline product which furnishes *dichlorotetrapyridinoruthenium chloride* (XIV) with hydrochloric acid.

$$[Ru(OH)Cl\,py_4]Cl \ (XIII.) \longrightarrow [RuCl_2\,py_4]Cl \ (XIV.)$$

$$[RuCl_2(NH_2Et)_4]Cl \ (XV.) \rightleftharpoons [Ru(OH)Cl(NH_2Et)_4]Cl \ (XVI.)$$

Ethylamine Analogue of Ruthenium Red.—Under conditions similar to those used for the production of "ruthenium red," ethylamine and ruthenium chloride react in aqueous media, giving a solution which, after acidification with hydrochloric acid, furnishes *dichlorotetraethylaminoruthenium chloride* (XV). This stable pink salt is converted into the less stable *chlorotetraethylaminohydroxoruthenium chloride* (XVI) by aqueous ammonia.

Ammonia is the only base of the four studied which furnishes an intensely coloured compound such as "ruthenium red." A possible explanation may be based on the view that cations of the foregoing compounds have an octahedral arrangement, consequently hydroxy (OH) and chloro (Cl) groups can occupy *cis-* or *trans-*positions relative to one another. Ammonia may induce one distribution of the hydroxy- and chloro-groups, whereas ethylenediamine, pyridine, and ethylamine favour the other configuration.

Experimental.

Ruthenium Trichloride.—Dry chlorine mixed with approximately 10% of carbon monoxide was passed over finely divided ruthenium at 380—420°, the metal speedily changing to a dark brown or black bulky powder. As soon as the absorption of chlorine had ceased the mixture was cooled in a slow stream of chlorine, this gas being finally displaced by dry nitrogen or carbon dioxide. In two typical experiments, 2·812 g. and 2·142 g. of ruthenium gave 5·460 g. (Found: Ru, 52·6; Cl, 47·1. Calc. for $RuCl_3$: Ru, 48·8; Cl, 51·2%), and 4·065 g. (Found: Ru, 50·1; Cl, 49·2%) respectively of chlorinated product. The preparations dissolved slowly in hot alcohol, forming green solutions and leaving small residues of metallic ruthenium.

The mixture of chlorine and carbon monoxide passed over ruthenium at 600° gave black lustrous dense crystals of ruthenium trichloride. The preparation was purer (Found: Ru, 49·2; Cl, 50·4%) than those obtained at the lower temperature, but was inert and was not used in the following experiments.

Action of Ammonia on Ruthenium Trichloride.—Pure dry ammonia, passed over ruthenium trichloride (1·0 g.) at 0°, was readily absorbed with generation of heat. The product was kept over caustic soda in an ammonia atmosphere in a desiccator (Found: Ru, 37·2, 40·1, 42·7; Cl, 39·9, 41·8, 44·0. $RuCl_3,4NH_3$ requires Ru, 36·8; Cl, 38·6%). The *amminated trihalide* partly dissolved in water to a deep red solution, but was insoluble in alcohol and other organic media.

Chlorotetramminohydroxoruthenium Chloride Hydrate [*Ruthenium Red* (I)].—Powdered ruthenium trichloride (2·0 g.) was added in small quantities to aqueous ammonia (*d* 0·880; 50 c.c.) at 0°. The mixture was left at room temperature for 12 hours, diluted with water, and heated at 90° until no more solid dissolved. The purple-red solution was filtered from ruthenium (0·1 g.), evaporated to 50 c.c., and diluted with alcohol (200 c.c.); the *amminated ruthenium chloride* was then precipitated in small purple crystals, which were further purified by solution in water and precipitation with alcohol. This and the following compounds were dried over sulphuric acid (Found: Ru, 36·8, 37·1, 37·4; Cl, 25·5, 25·2, 25·8; N, 20·35, 20·8; H_2O, 6·3. $H_{15}O_2N_4Cl_2Ru$ requires Ru, 36·9; Cl, 25·7; N, 20·3; H_2O, 6·5%). "Ruthenium red" dissolved in water to an intensely red solution, the colour being perceptible at dilutions of more than 1 in 10^6. Aqueous solutions soon decomposed at room temperature, more rapidly on heating, and gave a precipitate of black hydrated ruthenium oxide. These solutions were more stable in the presence of ammonia and ammonium chloride, very slow crystallisation leading to crystals of (I) having a fine coppery lustre. The well-dried tetrammine was stable under normal conditions, but lost a molecule of water at 150°; it did not decompose further below 200°.

Dichlorotetramminoruthenium Chloride Dihydrate (II).—The compound (I) (0·5 g.) in water (50 c.c.) was treated with concentrated hydrochloric acid (10 c.c.), the red colour of the solution instantly changing to brown. The mixture was warmed for several hours at 40—50°; the brown crystalline powder was then collected and washed with a little 2*N*-hydrochloric acid (Found: Ru, 32·8; Cl, 34·7; N, 17·7. $H_{16}O_2N_4Cl_3Ru$ requires Ru, 32·6; Cl, 34·1; N, 17·9%). This *amminated ruthenium* compound dissolved in water to a yellow solution, which became pink at high dilutions. Aqueous ammonia at once regenerated "ruthenium red" with this dichloro-derivative.

Chloronitratotetramminoruthenium Nitrate Tetrahydrate (III).—A concentrated solution of chlorotetramminohydroxoruthenium chloride (I) in water (20 c.c.) was treated with 2*N*-nitric acid (20 c.c.), and ammonium nitrate stirred into the deep brown solution. After 12 hours the brown leaflets were collected and air-dried (Found: Ru, 25·4; Cl, 9·1. $H_{20}O_{10}N_6ClRu$ requires Ru, 25·4; Cl, 8·8%). The *nitrate* gave the characteristic tint of "ruthenium red" with aqueous ammonia.

Dibromotetramminoruthenium Bromide Hydrate (V).—The compound (I) (1·0 g.) in water (75 c.c.) was treated with a large excess of concentrated aqueous potassium bromide and then, after heating for 1 hour, with constant-boiling hydrobromic acid (10 c.c.). The dark brown, crystalline precipitate was collected and washed with a little hydrobromic acid and alcohol (Found: Ru, 24·1; Br, 55·9. $H_{14}ON_4Br_3Ru$ requires Ru, 23·8; Br, 56·1%). This *tetrammine* was less soluble but possessed similar properties to the corresponding chlorine analogue (II).

Bromotetramminohydroxoruthenium Bromide Hydrate (IV).—The compound (V) was dissolved in concentrated aqueous ammonia, and alcohol was added to the filtered, deep purple solution. The *hydroxo-bromide*, which separated in small, deep purple crystals, was further purified by addition of alcohol to a concentrated aqueous solution (Found: Ru, 27·9; Br,

41·2. $H_{15}O_2N_4Br_2Ru$ requires Ru, 27·9; Br, 40·9%). It was similar in properties to the chlorine analogue.

Chlorotetramminohydroxoruthenium Iodide (VI).—A cold solution of (I) in water was treated with excess of a cold aqueous solution of potassium iodide. When alcohol was added to the well-stirred mixture, the *chloro-iodide* separated in small purple crystals (Found: Ru, 29·1. $H_{13}ON_4ClIRu$ requires Ru, 29·1%).

Iodotetramminohydroxoruthenium Iodide (VII).—An aqueous mixture containing (I) and excess of potassium iodide was heated and evaporated to crystallising point. The almost black crystals of the iodine analogue of "ruthenium red" were washed with aqueous potassium iodide and alcohol (Found: Ru, 24·5; I, 57·9. $H_{13}ON_4I_2Ru$ requires Ru, 23·1; I, 57·6%).

Di-iodotetramminoruthenium Iodide (VIII).—(a) The compound (VII) was triturated with hydriodic acid (Found: Ru, 18·8; I, 69·6. $H_{12}N_4I_3Ru$ requires Ru, 18·5; I, 69·1%). (b) A mixture of "ruthenium red" (I), potassium iodide, and 2*N*-sulphuric acid was evaporated to crystallisation point. The crystals were washed with a little water and alcohol (Found: Ru, 18·7%). Aqueous ammonia generated the hydroxo-iodide (VII) with this salt.

Chlorotetramminohydroxoruthenium Nitrosoruthenipentachloride (IX).—Aqueous solutions containing equivalent quantities of (I) and potassium nitrosoruthenipentachloride were mixed; the sparingly soluble, purple *salt* then separated and was washed with cold water and alcohol (Found: Ru, 41·2; Cl, 33·1. $H_{26}O_3N_9Cl_7Ru_3$ requires Ru, 40·6; Cl, 32·8).

Chlorotetramminohydroxoruthenium Platinochloride.—Aqueous solutions of (I) and potassium platinochloride were mixed; the reddish-purple microcrystalline deposit was washed with a small quantity of cold water and alcohol (Found: Ru + Pt, 50·7. $H_{26}O_2N_8Cl_6Ru_2Pt$ requires Ru + Pt, 51·0%).

Chlorobisethylenediaminohydroxoruthenium Chloride (X).—Ruthenium trichloride (2·0 g.) was added slowly to ethylenediamine (1·2 g.) in water (50 c.c.). After 12 hours, the mixture was diluted with water (50 c.c.) and heated at 90° for 4 days. The yellow filtrate was evaporated to 50 c.c. and diluted with alcohol; the *hydroxo-chloride* then separated as a microcrystalline powder, which was purified by precipitation from aqueous solution with alcohol (Found: Ru, 33·0; Cl, 23·3. $C_4H_{17}ON_4Cl_2Ru$ requires Ru, 32·8; Cl, 22·9%). The moist, freshly precipitated ruthenium compound was dark grey, but dried to a dark brown, crystalline powder, which dissolved in water to a reddish-yellow solution. The yellow alcoholic filtrate from the preparation of the ethylenediamine compound furnished a dark brown, viscid residue on evaporation, but a crystalline compound has not yet been obtained from this fraction. Analysis indicated a larger proportion of ethylenediamine (Ru, 23·9%) than that in chlorobisethylenediaminohydroxoruthenium chloride.

Dichlorobisethylenediaminoruthenium Chloride (XI).—An aqueous solution of the hydroxo-chloride (X) was treated with excess of 2*N*-hydrochloric acid and evaporated to crystallising point. The dark brown crystals were recrystallised from hydrochloric acid (Found: Ru, 30·8; Cl, 32·1. $C_4H_{16}N_4Cl_3Ru$ requires Ru, 31·0; Cl, 32·4%). This *chloride* dissolved in water to a yellow-brown solution and hydrolysed to the compound (X).

Iodobisethylenediaminohydroxoruthenium Iodide (XII).—An aqueous mixture of the compound (X) and potassium iodide was evaporated to crystallising point; the almost black crystals were collected and washed with a little water and alcohol (Found: Ru, 21·0; I, 51·9. $C_4H_{17}ON_4I_2Ru$ requires Ru, 20·6; I, 51·5%). This *iodide* was sparingly soluble in water and rather unstable.

Chlorotetrapyridinohydroxoruthenium Chloride (XIII).—Ruthenium trichloride (2·0 g.) was added to 30% aqueous pyridine (100 c.c.), and the mixture heated with occasional shaking for several days. The yellow needles were separated as far as possible from admixed ruthenium chloride and crystallised from aqueous pyridine (Found: Ru, 20·6; Cl, 14·5. $C_{20}H_{21}ON_4Ru$ requires Ru, 20·1; Cl, 14·1%).

Dichlorotetrapyridinoruthenium Chloride (XIV).—An aqueous solution of the compound (XIII) was treated with hydrochloric acid and evaporated to crystallising point (Found: Ru, 19·6. $C_{20}H_{20}N_4Cl_3Ru$ requires Ru, 19·4%).

Dichlorotetraethylaminoruthenium Chloride (XV).—Ruthenium trichloride (2·0 g.) was slowly added to 30% aqueous ethylamine (50 c.c.) at 0°. After 12 hours the mixture was diluted with water (50 c.c.) and heated at 90° for 6 hours. The filtered solution was acidified with 2*N*-hydrochloric acid and evaporated to crystallising point. The mixture was triturated with alcohol, and the insoluble pink crystals recrystallised from dilute hydrochloric acid (Found: Ru, 26·1; Cl, 27·0. $C_8H_{28}N_4Cl_3Ru$ requires Ru, 26·2; Cl, 27·4%). This *ethylamine* derivative gave an orange-yellow solution in water, but was practically insoluble in alcohol.

Chlorotetraethylaminohydroxoruthenium Chloride (XVI).—The compound (XV) was dissolved in a small quantity of cold concentrated aqueous ammonia; the *hydroxo*-compound was then precipitated from the red solution by the addition of alcohol. The amorphous product was collected, dissolved in cold water, and again precipitated with alcohol (Found: Ru, 27·2; Cl, 18·8. $C_8H_{29}ON_4Cl_2Ru$ requires Ru, 27·5; Cl, 19·2%). This unstable ruthenium compound dissolved in water to a deep brownish-yellow solution, and hydrochloric acid regenerated the dichloro-compound (XV).

We are indebted to the Mond Nickel Co. for the loan of the ruthenium used in this investigation.

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10. *Studies in Dielectric Polarisation. Part XIV. The Dipole Moments of Ethyl, Phenyl, and α- and β-Naphthyl* iso*Cyanates.*

By ERIC G. COWLEY and JAMES R. PARTINGTON.

PART IV of this series (J., 1932, 2825) recorded the dipole moments of the alkyl *iso*thiocyanates measured in benzene solution; it was found that a linear structure satisfactorily accounted for the magnitude of the moments, and the Raman spectra of these compounds (Langseth, Nielsen, and Sørensen, *Z. physikal. Chem.*, 1934, *B*, **27**, 100) have confirmed this conclusion. The work has now been extended to the *iso*cyanates, for which, again, a linear structure is indicated (Cowley and Partington, *Nature*, 1935, **135**, 1038). The present paper describes the moments of ethyl, phenyl, and α- and β-naphthyl *iso*cyanates, the values found in benzene being 2·81, 2·28, 2·30, and 2·34 respectively (Debye units are used throughout). The moment of phenyl *iso*cyanate had previously been found to be 2·23 at 25° in benzene (Sidgwick, Sutton, and Thomas, J., 1933, 406) and 2·34 at 18° in carbon tetrachloride (Eide and Hassel, *Tidsskr. Kjemi Berg.*, 1930, **10**, 93), but no data are available for the other compounds.

Phenyl and α-naphthyl *iso*cyanates have approximately the same moment, that of β-naphthyl *iso*cyanate being somewhat greater. These results are similar to those for the corresponding halogen compounds, as is shown by the following values for the moments determined in benzene: chlorobenzene 1·56 (Smyth, Morgan, and Boyce, *J. Amer. Chem. Soc.*, 1928, **50**, 1536); α-chloronaphthalene 1·59 (Parts, *Z. physikal. Chem.*, 1930, *B*, **10**, 264), 1·50 (Nakata, *Ber.*, 1931, **64**, 2059); β-chloronaphthalene 1·72 (Parts, *loc. cit.*), 1·57 (Nakata, *loc. cit.*). The values (in benzene) for phenol and α- and β-naphthol, *viz.*, 1·73 (Smyth and Morgan, *J. Amer. Chem. Soc.*, 1927, **49**, 1030), 1·0, and 1·3 (Puchalik, *Physikal. Z.*, 1932, **33**, 341) respectively, show a different behaviour.

The moment of the *iso*cyanate group is greater in the aliphatic than in the aromatic series, and this is parallel to the behaviour of the *iso*thiocyanate group. In both groups the resultant moment acts in the same sense, the oxygen or the sulphur atom being at the negative end of the dipole, since the sign of the moment is the same as that of the C–Cl dipole.

The dipole moments of the *iso*thiocyanates are larger than those of the *iso*cyanates, owing to the fact that the C=S is greater than the C=O moment; this excess is shown below for corresponding members of the two series, the solvent being benzene in every case:

Ethyl *iso*thiocyanate	3·31 [1]	Phenyl *iso*thiocyanate	3·00 [3]	2·76 [3a]
Ethyl *iso*cyanate	2·81 [2]	Phenyl *iso*cyanate	2·28 [2]	
Difference	0·50	Difference	0·72	0·48
Thiobenzophenone	3·37 [4]	Dianisyl thioketone	4·44 [5]	
Benzophenone	2·95 [6]	Dianisyl ketone	3·90 [5]	
Difference	0·42	Difference	0·54	

[1] Hunter and Partington, J., 1932, 2825. [2] Present research.
[3] Bergmann and Tschudnowsky, *Z. physikal. Chem.*, 1932, *B*, **17**, 100; [3a] Bergmann, Engel, and Sandor, *ibid.*, 1930, *B*, **10**, 397.
[4] Hunter and Partington, J., 1933, 87.
[5] Donle and Volkert, *Z. physikal. Chem.*, 1930, *B*, **8**, 60 (both moments corrected for P_A).
[6] Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446.

The linear structure of the *iso*thiocyanates (see above) is in agreement with the fact that the moment shows an increase from the methyl to the ethyl compound. The nitrogen atom in the *iso*thiocyanates and *iso*cyanates is similarly linked, so that it is probable that the configuration of the valency bonds will be the same in the two groups. In both series the approximate additivity of the group moments in the *p*-substituted *iso*thiocyanates (Bergmann and Tschudnowsky, *loc. cit.*) and *iso*cyanates (Sidgwick, Sutton, and Thomas, *loc. cit.*) is in agreement with the linear structure of the groups. In Part IV (*loc. cit.*), an approximate value of the moment of ethyl *iso*thiocyanate was calculated, and a similar method has been applied to the *iso*cyanates and *iso*thiocyanates by Sutton (*Trans. Faraday Soc.*, 1934, **30**, 789). It has been concluded (Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293; Sutton, *loc. cit.*), from a consideration of the interatomic distances, that resonance probably occurs in the *iso*cyanate group. Of two possible structures, (I) and (II), for these com-

$$\underset{(I.)}{R{-}N{=}C{=}X} \qquad \underset{(II.)}{R{-}N{\equiv}C{\rightarrow}X} \qquad \underset{(III.)}{R{-}N{\leftarrow}C{\equiv}X}$$

pounds, (I) is excluded since it would not be linear. As, however, a molecule of the type (II) would have a large moment (> 6) whereas the observed moments are in approximate agreement with those calculated for the ordinary structure (I) alone, there must also be resonance with third form (III), which would be present in a quantity equal to that of form (II) to counterbalance the moment of the latter. This conclusion is supported by the values of the energy of these molecules (Pauling and Sherman, *J. Chem. Physics*, **1933**, **1**, 606). The absorption spectra of these compounds have been studied by Sho-Chow Woo and Ta-Kong Liu (*ibid.*, 1935, **3**, 544), who find that the *iso*cyanates are probably represented by (I), in spite of the fact that the characteristic absorption of the keto-group is absent.

Goubeau (*Ber.*, 1935, **68**, 912) now finds that the Raman spectra indicate that the N=C=O group in the *iso*cyanic esters is linear, and this conclusion is fully supported by the values of the dipole moments.

Experimental.

Apparatus.—The apparatus and experimental method are identical with those previously described (Cowley and Partington, J., 1935, 604).

Materials.—Kahlbaum's " thiophen-free " benzene, which had been dried by sodium and fractionated, was used as solvent.

Ethyl *iso*cyanate was prepared by heating potassium cyanate with potassium ethylsulphate. The product was fractionated to remove cyanurate, dried with anhydrous sodium sulphate, and twice fractionated. Owing to the instability of this substance, the measurements were made immediately. Methyl *iso*cyanate could not be obtained sufficiently pure for measurement. Phenyl *iso*cyanate (Kahlbaum) was dried and fractionated. The naphthyl *iso*cyanates were obtained from Fraenkel and Landau, Berlin. Great care was taken to avoid contact of the substances with air, as they are easily decomposed by moisture. The physical constants of the specimens were :

Compound.	B. p.	$D_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.
Ethyl *iso*cyanate	59·8°/759 mm.	0·9031	1·3808
Phenyl *iso*cyanate	161·7/752 mm.	1·0946	1·5363
α-Naphthyl *iso*cyanate	267·0/761 mm.	1·1774	—
β-Naphthyl *iso*cyanate	(m. p.) 56·4°	—	—

These figures may be compared with the following previous determinations upon *iso*cyanates : Phenyl, $D_{4^\circ}^{19\cdot6^\circ}$ 1·0956, $n_D^{19\cdot6^\circ}$ 1·5368 (Brühl, *Z. physikal. Chem.*, 1895, **16**, 216), b. p. 162° (Sidgwick, Sutton, and Thomas, *loc. cit.*); α-naphthyl, b. p. 269—270° (Hofmann, *Ber.*, 1870, **3**, 658); β-naphthyl, m. p. 55—56° (Vittenet, *Bull. Soc. chim.*, 1899, **21**, 958).

Results.—Solvent, benzene. All measurements at 20°.

Ethyl *iso*cyanate.

f_2.	ε.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·280	0·8789	26·57	—
0·007563	2·364	0·8790	27·74	181·3
0·026562	2·575	0·8794	30·49	174·1
0·034291	2·660	0·8795	31·52	170·9
0·043812	2·770	0·8798	32·80	168·8
0·050951	2·846	0·8799	33·64	165·3

$P_{2\infty}$ = 185·0 c.c.; P_E = 18·3 c.c.;
$P_{2\infty} - P_E$ = 166·9 c.c.; μ = 2·81.

Phenyl *iso*cyanate.

f_2.	ε.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·280	0·8789	26·57	—
0·009412	2·351	0·8812	27·65	141·3
0·018163	2·418	0·8833	28·64	140·5
0·029040	2·500	0·8861	29·82	138·5
0·043582	2·607	0·8896	31·32	135·6
0·051078	2·667	0·8917	32·04	133·7

$P_{2\infty}$ = 144·0 c.c.; P_E = 33·9 c.c.;
$P_{2\infty} - P_E$ = 110·1 c.c.; μ = 2·28.

α-Naphthyl *iso*cyanate.

f_2.	ε.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·279	0·8788	26·56	—
0·006963	2·336	0·8821	27·49	160·2
0·008945	2·352	0·8829	27·76	160·7
0·025254	2·485	0·8906	29·88	158·0
0·029829	2·522	0·8930	30·45	157·0

$P_{2\infty}$ = 161·5 c.c.; P_E = 49·3 c.c.;
$P_{2\infty} - P_E$ = 112·2 c.c.; μ = 2·30.

β-Naphthyl *iso*cyanate.

f_2.	ε.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·279	0·8788	26·56	—
0·005664	2·327	0·8816	27·34	164·3
0·014629	2·402	0·8860	28·54	161·9
0·015443	2·409	0·8865	28·65	161·9
0·026259	2·499	0·8917	30·07	160·2

$P_{2\infty}$ = 165·5 c.c.; P_E = 49·3 c.c.;
$P_{2\infty} - P_E$ = 116·2 c.c.; μ = 2·34.

SUMMARY.

The dipole moments in Debye units of ethyl (2·81), phenyl (2·28), α-naphthyl (2·30), and β-naphthyl (2·34) *iso*cyanates, measured in benzene solution at 20°, are in agreement with a linear structure for the *iso*cyanate group. It is pointed out that this conclusion is supported by the Raman spectra of these compounds. It is shown that the *iso*cyanate and the *iso*thiocyanate group are similar in configuration.

QUEEN MARY COLLEGE, LONDON, E. 1. [*Received, October 22nd,* 1935.]

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11. *Studies in Dielectric Polarisation. Part XV. The Dipole Moments of Five-membered Nitrogen Ring Compounds : Indole, Skatole, Carbazole, Isatin, Phthalimide, and Succinimide.*

By ERIC G. COWLEY and JAMES R. PARTINGTON.

ALTHOUGH numerous determinations of the moments of six-membered nitrogen ring compounds have been made, the only existing data for five-membered rings containing nitrogen are those for pyrrole and *N*-methylpyrrole (Part XI, J., 1933, 1259; Jackson, *Trans. Faraday Soc.*, 1934, **30**, 800). We have therefore determined the moments of the analogous compounds indole, skatole, and carbazole, and also those of isatin, phthalimide, and succinimide for comparison. We find that the dipole moment increases from pyrrole to indole, but there is then a smaller increase to carbazole. The values of the dipole moments found (in Debye units) are summarised below, together with relevant data of other authors.

Compound.	μ.	Compound.	μ.
Pyrrole	1·83,[1] 1·78[2]	Pyridine	2·11,[4] 2·21,[5] 2·26[6]
N-Methylpyrrole	1·94[2]	*iso*Quinoline	2·53,[5] 2·52,[7] 2·54[8]
Indole	2·05[3]	Quinoline	2·25,[6] 2·14,[5] 2·18,[7] 2·16[8]
Skatole	2·08[3]	—	—
Carbazole	2·09[3]	Acridine	1·95[5]
Isatin	5·72[3]	Succinimide	1·54[3]
		Phthalimide	2·10[3]

References: [1] Cowley and Partington, J., 1933, 1259 (solvent, benzene). [2] Jackson, *loc. cit.* (solvent not stated). [3] Present research (indole and skatole in benzene; other compounds in dioxan). [4] Lange, *Z. Physik*, 1925, **33**, 169 (solvent, benzene). [5] Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446 (solvent, benzene). [6] Rolinski, *Physikal. Z.*, 1928, **29**, 658 (solvent, benzene). [7] Le Fèvre and Smith, J., 1932, 2810 (solvent, benzene). [8] Rau and Narayanaswamy, *Z. physikal. Chem.*, 1934, *B*, **26**, 23 (solvent, benzene).

The three compounds pyrrole, indole, and carbazole are very similar in general properties. Chemically, they all exhibit both acidic and basic properties, and the stability

increases as the series is ascended. These five-membered nitrogen rings present a comparatively simple case for consideration of the dipole moments, for the regular five-membered ring is flat and the intervalency angles are nearly tetrahedral. This will be approximately the case in the above compounds, the hydrogen atom of the imino-group lying out of the plane of the ring. An approximate calculation of the moment of pyrrole can be made from the following data. In the ammonia molecule the distances are (Mecke, "Structure of Molecules," ed. Debye, 1932, 30) : N–H 0·977, H–H 1·43, height of pyramid 0·517 Å.; hence it follows that the angle between one of the N–H bonds and the plane of the other two is 96° 30′. If the moment of the $\overrightarrow{\mathrm{C{-}N}}$ bond is taken as 0·6, from that of trimethylamine 0·6 (Steiger, *Physikal. Z.*, 1931, **32**, 425; vapour measurement) with no allowance for the methyl group, and the angle of the C–N–C bonds is taken as 108° in pyrrole, the resultant moment of the two C–N moments is vectorially added to that of the $\overleftarrow{\mathrm{N{-}H}}$ moment, taken as 1·5 from that of ammonia (Watson, *Proc. Roy. Soc.*, 1927, *A*, **117**, 43; vapour measurement). This gives the moment of pyrrole as 1·58, which can be considered as reasonably near the experimental value 1·83, in view of the fact that the influence of the double bonds and the ring has not been allowed for, and also of the uncertainty in the angles. It can be shown that the moment of pyrrole will act in the line joining the nitrogen nucleus and the mid-point of the opposite side of the ring at an angle of about 70° to the plane of the ring.

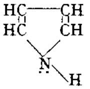
The higher moment of indole than of pyrrole reflects the influence of the benzene ring. The further increase from indole to carbazole is much smaller. These results are compared in the above table with those for the six-memhered rings. It is seen that this change in moment is paralleled by the results for pyridine and quinoline. In view of the results of von Auwers and Kraul (*Ber.*, 1925, **58**, 543), which indicate that the acridine molecule contains seven double links, the structure with a para-bond can be eliminated, and the lower moment of acridine than of pyridine and quinoline is therefore unexpected. The fact that the moment of skatole (β-methylindole) differs but little from that of indole would be expected.

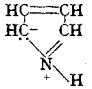
Isatin is generally regarded as being diketonic in the free state and in acid solution. Its structure cannot be definitely deduced from the available data for the absorption spectra of this compound and its *N*- and *O*-ethers, since the conclusions of Hartley and Dobbie, (*J.*, 1899, **75**, 640) and Dabrowski and Marchlewski, (*Bull. Soc. chim.*, 1933, **53**, 946) have not been supported by other authors (Morton and Rogers, J., 1925, **127**, 2698; Ault, Hirst, and Morton, J., 1935, 1653), although the spectrum of isatin resembles that of its *N*-methyl ether rather than that of its *O*-methyl ether. The large value of the dipole moment, however, can be most easily explained by the diketonic formula. From a consideration of the moment of indole, 2·05, and of the keto-group, 3·0 (from the moment of benzophenone; Fuchs and Donle, *Z. physikal. Chem.*, 1933, *B*, **22**, 1), and their respective positions on the ring, it can be calculated that the moment of isatin would be large, and that of the isomeric phthalimide much smaller : the values now found, *viz.*, 5·72 and 2·10 respectively, are in agreement with this calculation.

Succinimide has a lower moment than phthalimide, and this leads to the conclusion that the five-membered ring containing nitrogen and also the two keto-groups has a large polarising influence on the benzene ring. Rau and Narayanaswamy (*loc. cit.*) find that the moments of the derivatives of pyridine and quinoline, calculated on the assumption that the C–N bond has a moment of 1·3, are in good agreement with the observed figures for these compounds. Since the C–N moment was deduced from the nitrile group moment, however, these calculations are open to objection, for it has been shown (*e.g.*, Sidgwick, "The Covalent Link in Chemistry," 1933, p. 153) that the increase of the moment of a multiple link over that of the corresponding single link is greater than would be expected from the number of links.

The energies of the pyrrole, indole, and carbazole molecules have been examined by Pauling and Sherman (*J. Chem. Physics*, 1933, **1**, 606), who compared the heats of formation E of the various possible electronic structures of different molecules with the heat of formation E' calculated for the usual structure. The difference $E - E'$ may be interpreted

as the resonance energy of the molecule among these electronic structures. The differences are for pyrrole 0·98, indole 2·34, and carbazole 3·93 volt-electrons. Pauling and Sherman, therefore, postulate that the large resonance energy requires that, in addition to the ordinary form of pyrrole (I), other structures contribute strongly to the normal state of the molecule, the four of the type (II) being the most reasonable, since a negative carbon atom, with three shared and one unshared pair of electrons, occurs in other structures. The resonance energies of indole and carbazole are both a little lower respectively than the energies of (i) pyrrole plus benzene and (ii) pyrrole plus twice that of benzene, as would be expected since the sharing of atoms by both rings partially inhibits resonance.

(I.) 

 (II.)

The effect of these excited structures on the dipole moment of pyrrole has been considered by Sutton (*Trans. Faraday Soc.*, 1934, **30**, 799), but further work on the substituted pyrroles is necessary in order to obtain more definite evidence on this question.

Experimental.

The apparatus and method of calculation were those of the previous paper.

Materials.—All the compounds used were obtained from Kahlbaum and had the following m. p.'s: indole 52·5°, skatole 95·1°, carbazole 245·0°, isatin 201·0°, phthalimide 238·0°. Succinimide was heated in a vacuum and twice recrystallised from anhydrous acetone; m. p. 125·0°.

Kahlbaum's "thiophen-free" benzene, which had been dried by sodium and fractionated, was used as solvent for indole and skatole. The solubility of the other compounds in benzene was too low to allow moments to be measured, so these were determined in dioxan. The dioxan (B.D.H.), which had been purified by treatment with sodium wire until no further action took place, was fractionated several times and finally frozen out. It was always dried and fractionated before each measurement. The dielectric constants of the specimens of dioxan used were little different from that of benzene, so that the comparison of the moments in the two solvents is justifiable. All the measurements were made at 20°.

Measurements in benzene solution.

Indole.

f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·279	0·8786	26·56	—
0·006295	2·320	0·8804	27·18	125·1
0·014449	2·375	0·8830	27·99	125·5
0·023030	2·433	0·8855	28·83	125·1
0·028441	2·460	0·8871	29·34	124·3

$P_{2\infty}$ = 125·7 c.c.; P_E = 36·5 c.c.; $P_{2\infty} - P_E$ = 89·2 c.c.; μ = 2·05.

Skatole.

f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·279	0·8786	26·56	—
0·006850	2·324	0·8806	27·27	130·2
0·015841	2·379	0·8832	28·14	126·3
0·024339	2·430	0·8858	28·92	123·5
0·027826	2·450	0·8868	29·23	122·5

$P_{2\infty}$ = 132·5 c.c.; P_E = 41·1 c.c.; $P_{2\infty} - P_E$ = 91·4 c.c.; μ = 2·08.

Measurements in dioxan solution.

Carbazole.

f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·237	1·0325	24·90	—
0·007559	2·293	1·0345	25·80	144·0
0·016210	2·355	1·0365	26·82	144·3
0·021625	2·395	1·0375	27·45	142·8
0·027953	2·440	1·0391	28·18	142·2

$P_{2\infty}$ = 144·6 c.c.; P_E = 51·8 c.c.; $P_{2\infty} - P_E$ = 92·8 c.c.; μ = 2·09.

Isatin.

f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·237	1·0328	24·90	—
0·006209	2·550	1·0355	29·10	701·3
0·010335	2·768	1·0374	31·70	682·9
0·012977	2·908	1·0388	33·25	668·4
0·017953	3·177	1·0407	36·02	644·3

$P_{2\infty}$ = 731·9 c.c.; P_E = 40·4 c.c.; $P_{2\infty} - P_E$ = 691·5 c.c.; μ = 5·72.

Phthalimide.

f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·243	1·0324	24·99	—
0·005255	2·280	1·0342	25·56	133·5
0·008962	2·307	1·0359	25·96	133·2
0·014725	2·349	1·0381	26·58	133·0
0·018699	2·378	1·0395	27·00	132·5

$P_{2\infty}$ = 133·7 c.c.; P_E = 40·4 c.c.; $P_{2\infty} - P_E$ = 93·3 c.c.; μ = 2·10.

Succinimide.

f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·244	1·0326	25·00	—
0·005860	2·266	1·0342	25·29	75·6
0·012737	2·292	1·0362	25·63	74·5
0·017458	2·310	1·0375	25·86	74·3
0·022599	2·330	1·0389	26·16	74·1

$P_{2\infty}$ = 76·0 c.c.; P_E = 25·6 c.c.; $P_{2\infty} - P_E$ = 50·4 c.c.; μ = 1·54.

SUMMARY.

The following moments (in *D*) have been measured and the results discussed: indole 2·05, and skatole 2·08, in benzene; carbazole 2·09, isatin 5·72, phthalimide 2·10, and succinimide 1·54, in dioxan.

We thank the Chemical Society and the Dixon Fund for grants, and one of us (E. G. C.) is indebted to the University of London for the award of a Postgraduate Studentship.

QUEEN MARY COLLEGE, LONDON, E. 1. [*Received, October 22nd*, 1935.]

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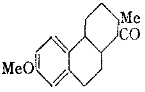
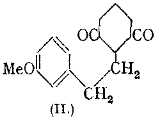
12. *The Synthesis of Compounds related to the Sterols, Bile Acids, and Oestrus-producing Hormones. Part VIII.*

By C. L. HEWETT.

IN Part I (Cook and Hewett, J., 1933, 1105) comment was made on the difficulties experienced in synthesising the sterol type of ring system from 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene, and the view was expressed that these difficulties would be overcome by the use of analogous derivatives of *as*-octahydrophenanthrene. This view has been accepted by Robinson and Schlittler (J., 1935, 1288), who state "one of the more promising methods for the synthesis of oestrone and related substances depends in principle on the appropriate modification of such an intermediate as the ketomethoxymethyloctahydrophenanthrene" (I).



(I.)



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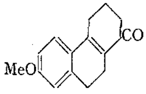
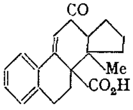


(III.)



(IV.)

Methods of synthesis of compounds of type (I) are under investigation in this laboratory, and in view of the paper by Robinson and Schlittler, preliminary experiments in connection with one such method (compare Cohen and Cook, J., 1935, 1571) are recorded.

The condensation of dihydroresorcinol with benzyl chloride, β-1-naphthylethyl bromide, and β-m-*methoxyphenylethyl bromide* has been studied, as the formation of the *C*-alkyl compounds (II) would give a simple route to polycyclic ketones of the desired type. With benzyl chloride *C*-alkylation took place to a reasonable extent, but with β-1-naphthylethyl bromide *O*-alkylation occurred almost exclusively. From β-*m*-methoxyphenylethyl bromide the *O-alkyl* compound was mainly formed, but there was also obtained a small yield of β-*m*-methoxyphenylethyl*cyclo*hexane-2 : 6-dione (II), the properties of which agree with those given for this compound by Robinson and Schlittler. By cyclisation of (II) with 80% sulphuric acid at 100°, 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene (III) was rapidly formed in good yield, this method being preferable to that used by Robinson and Schlittler.

The predominating *O*-alkylation of dihydroresorcinol renders the method unsuitable for preparative purposes. The method of Robinson and Schlittler is lengthy, and a promising simpler method is under investigation.

Preliminary attempts have also been made to utilise the Michael reaction for the synthesis of polycyclic compounds related to oestrone. For example, the condensation of ethyl β-phenylethylmalonate with 2-acetyl-1-methyl-Δ^1-*cyclo*pentene (prepared from methyl-Δ^1-*cyclo*pentene by the method of Darzens, *Compt. rend.*, 1910, **150**, 707) led to the isolation in small yield of an *acid*, the analysis of which suggested that it was represented by (IV). This experiment was made before it was known that the quaternary methyl group of oestrone is at C_{13} and not at C_{14}, and the investigation of (IV) has not been pursued.

Experimental.

m-*Bromoanisole.*—Conversion of *m*-bromoaniline into *m*-bromphenol by the method of Diels and Bunzl (*Ber.*, 1905, **38**, 1495) gave poor yields and the following modification was adopted: To a solution of *m*-bromoaniline (100 g.) in methyl alcohol (500 c.c.) at 0°, concentrated sulphuric acid (65 c.c.) was added very slowly, followed by amyl nitrite (76 g.). After 1 hour the diazonium sulphate was washed with alcohol and ether, dissolved in ice-cold water, and added to boiling *N*-sulphuric acid (1 l.). Ether extracted *m*-bromphenol (60 g.), b. p. 120° (vacuum of the water-pump). This (170 g.) was heated on the water-bath for 3 hours with 10% potassium hydroxide solution (650 c.c.) and methyl *p*-toluenesulphonate (230 g.). The bromoanisole was distilled in steam after the addition of 150 c.c. of 10% potassium hydroxide solution. Yield, 154 g. after vacuum distillation.

β-m-*Methoxyphenylethyl Bromide.*—To an ice-cold Grignard solution prepared from *m*-bromoanisole (90 g.), magnesium (12 g.), and ether (500 c.c.) was added ethylene oxide (25 g.) diluted with ether (50 c.c.) (compare Shoesmith and Connor, J., 1927, 2233). After standing overnight, the ether was distilled off, and the residue heated at 100° for 1 hour. It was then decomposed with ice and hydrochloric acid, and the product was extracted with ether, washed, dried, and fractionated in a vacuum, giving 43 g. of the alcohol, b. p. 150—155°/18 mm. The 3 : 5-*dinitrobenzoate* separated from alcohol in pale yellow, prismatic needles, m. p. 106·5—107·5° (Found: C, 55·8; H, 4·5. $C_{16}H_{14}O_7N_2$ requires C, 55·5; H, 4·1%). Phosphorus tribromide (25 g.) was rapidly added to the alcohol (37·5 g.), dissolved in carbon tetrachloride (50 c.c.) previously warmed to 60°, and the whole was refluxed for 15 minutes. The solution was then cooled, washed with water and dilute aqueous sodium carbonate (to remove acid phosphite ester), dried, and distilled, giving β-m-*methoxyphenylethyl bromide* (34·5 g.) as an almost colourless liquid, b. p. 138°/12 mm. (Found: C, 50·75; H, 5·3. $C_9H_{11}OBr$ requires C, 50·2; H, 5·2%).

Dihydroresorcinol Condensations.—Dihydroresorcinol and "molecular" potassium in benzene gave a red resinous product and the condensations were therefore effected by sodium ethoxide. Sodium (1 mol.) was dissolved in ethyl alcohol (25 c.c. per g. of sodium), dihydroresorcinol (1 mol.) and the halide (1 mol.) added, and the whole boiled under reflux (3 hours in the case of benzyl chloride; 24 hours in the other two cases). The alcohol was then removed, water added, and the neutral part removed by extraction with ether; this consisted of unchanged halide and the *O*-alkyl compound. The alkaline solution on acidification with dilute sulphuric acid yielded the *C*-alkyl compound.

(i) *Condensation with benzyl chloride.* The precipitate from the alkaline solution crystallised from aqueous alcohol (charcoal) in colourless needles of *benzyl*cyclo*hexane*-2 : 6-*dione*, m. p. 184—185° (yield, 1·9 g. from 6·3 g. of benzyl chloride) (Found: C, 76·9; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·1; 7·0%). In an attempt to effect ring closure to a fluorene derivative by concentrated sulphuric acid at − 15° the diketone was converted into a *sulphonic acid*, which crystallised from aqueous acetic acid in pink rhombic tablets, m. p. 193—194° (Found: C, 52·5; H, 5·65. $C_{13}H_{14}O_5S,H_2O$ requires C, 52·0; H, 5·4%). The diketone (0·2 g.) was recovered unchanged after boiling for 1 hour with potassium hydroxide (0·2 g.) in aqueous alcohol.

(ii) *Condensation with* β-1-*naphthylethyl bromide* (28·2 g.). Acidification of the alkaline solution and extraction with ether yielded 1·2 g. of a mixture of oil and crystals which could not be purified. The neutral fraction when washed with ether gave a sparingly soluble, crystalline solid, which was recrystallised from alcohol (yield, 10 g.). 3-*Keto*-Δ[1]-cyclo*hexenyl* β-1-*naphthylethyl ether* formed colourless silky needles, m. p. 138—139°, insoluble in dilute alkali solution (Found: C, 80·8; H, 6·8. $C_{18}H_{18}O_2$ requires C, 81·15; H, 6·8%).

An attempt to make the oxime of this keto-ether (0·3 g.) with hydroxylamine hydrochloride (0·3 g.) and pyridine (3 c.c.) at 100° resulted in hydrolysis to β-1-naphthylethyl alcohol, which was also obtained when the ether (0·5 g.) was hydrolysed with potassium hydroxide (0·5 g.) in aqueous alcohol on the water-bath for 1 hour.

(iii) *Condensation with* β-m-*methoxyphenylethyl bromide.* Acidification of the alkaline solution gave β-*m*-methoxyphenylethyl*cyclo*hexane-2 : 6-dione (II), m. p. 149—150° after crystallisation from alcohol (Robinson and Schlittler, *loc. cit.*, give m. p. *ca.* 150°). Yield, 0·3 g. from 6·3 g. of bromide (Found: C, 73·5; H, 7·7. Calc.: C, 73·2; H, 7·3%).

The neutral fraction from the condensation was distilled and the fraction, b. p. 205—207°/0·5 mm., was collected and redistilled. The β-m-*methoxyphenylethyl* ether of dihydroresorcinol formed a colourless viscous liquid, b. p. 205—207°/0·5 mm. (Found: C, 72·85; H, 7·45. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%).

β-*m*-Methoxyphenylethyl*cyclo*hexane-2 : 6-dione (100 mg.) was heated on the water-bath with 80% sulphuric acid (10 parts) for 5 minutes, the product poured into water and extracted with ether, and the ethereal solution washed with dilute aqueous sodium carbonate, dried, and evaporated. The residual syrup was converted into the 2 : 4-dinitrophenylhydrazone (of III), m. p. 253—255° after recrystallisation from xylene (90 mg.) (Robinson and Schlittler give 256°) (Found : C, 62·2; H, 5·0. Calc. : C, 61·8; H, 4·9%).

*Condensation of Ethyl β-Phenylethylmalonate with 2-Acetyl-1-methyl-Δ¹-*cyclo*pentene.*—Into a well-cooled solution (– 10°) of anhydrous stannic chloride (6·5 g.) in carbon disulphide (150 c.c.) was slowly dropped a mixture of acetyl chloride (19·6 g.) and Δ¹-methyl*cyclo*pentene (20·5 g.; Skraup and Binder, *Ber.*, 1929, **62**, 1135). After 5 hours at 0°, ice and hydrochloric acid were added and the carbon disulphide layer was washed with dilute hydrochloric acid and water. The solvent was removed (after the addition of 1 mol. of dimethylaniline) and the residue was heated at 180° for 3 hours, cooled, diluted with ether, washed with dilute hydrochloric acid and water, dried, and evaporated. Distillation gave 10·5 g. of a colourless liquid, b. p. 115°/11 mm.

To a solution of sodium (0·8 g.) in alcohol (11·3 c.c.), ethyl β-phenylethylmalonate (Horne and Shriner, *J. Amer. Chem. Soc.*, 1933, **55**, 4653) (9·2 g.) was added, followed by 2-acetyl-1-methyl-Δ¹-*cyclo*pentene (4·3 g.), prepared as described above. The whole was boiled for 24 hours, diluted with water, and washed with ether. The aqueous layer was then acidified and the solid which was precipitated was extracted with a large volume of ether. After evaporation of the ether, the residue was crystallised from methyl alcohol, and then from acetic acid, forming almost colourless plates (0·6 g.), m. p. 242° (Found : C, 76·9; H, 6·7. $C_{19}H_{26}O_3$ requires C, 76·9; H, 6·75%). This *acid*, (probably IV) was soluble in boiling dilute sodium carbonate solution, from which the sodium salt separated in needles on cooling.

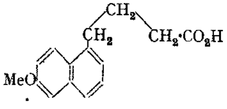
The Research Institute of the Cancer Hospital (Free),
London, S.W. 3.
[*Received, November 12th*, 1935.]

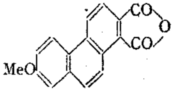
13. *The Synthesis of Compounds related to the Sterols, Bile Acids, and Oestrus-producing Hormones. Part IX.*

By A. Cohen, J. W. Cook, and C. L. Hewett.

As a preliminary to the synthesis of 7-methoxyphenanthrene-1 : 2-dicarboxylic anhydride, which from its relationship to the degradation products of oestriol methyl ether (MacCorquodale, Levin, Thayer, and Doisy, *J. Biol. Chem.*, 1933, **101**, 753) might be expected to have oestrogenic properties, we intended to study the cyclisation of ethyl α-oxalyl-γ-1-naphthylbutyrate, a reaction analogous to the synthesis of 3 : 4-dihydronaphthalene-1 : 2-dicarboxylic acid by Auwers and Möller (*J. pr. Chem.*, 1925, **109**, 124), to which we directed attention in Part 1 (J., 1933, 1106). After some unsatisfactory attempts to simplify the preparation of the required type of oxalyl ester by condensation of β-naphthylethyl bromide with ethyl oxalacetate, our experiments were anticipated by Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1935, **57**, 1508), who synthesised 3 : 4-dihydrophenanthrene-1 : 2-dicarboxylic anhydride. In view of the high oestrogenic activity subsequently reported for this compound (*idem, ibid.*, p. 1852) we returned to our original objective and have synthesised *7-methoxyphenanthrene-1 : 2-dicarboxylic anhydride* (II), which we also required for comparison with a sample prepared by one of us by a much simpler method (Cohen, *Nature*, 1935, **136**, 869).

γ-(6-Methoxy-1-naphthyl)butyric acid (I) was obtained by condensing β-(6-methoxy-1-naphthyl)ethyl bromide (Cohen, Cook, and Hewett, J., 1935, 452) with ethyl malonate, with subsequent hydrolysis and decarboxylation.

(I.)




(II.)

The succeeding stages were exactly analogous to those used by Fieser and Hershberg, and require no further comment. The results of tests for oestrogenic activity will be reported elsewhere.

Experimental.

β-(6-*Methoxy*-1-*naphthyl)ethylmalonic Acid*.—A solution of β-6-methoxy-1-naphthylethyl bromide (15 g.) in toluene (15 c.c.) was added to the potassio-compound prepared from ethyl malonate (18 g.) and powdered potassium (3·75 g.) in toluene (50 c.c.). The whole was heated at 120—130° for 55—60 hours, and the substituted malonic ester was isolated in the usual manner, b. p. 200—205°/0·3 mm. (13·7 g.). Hydrolysis of this ester with boiling aqueous-alcoholic potash (3 hours) gave β-(6-*methoxy*-1-*naphthyl)ethylmalonic acid*, which crystallised from water in lustrous colourless leaflets, m. p. 160° (with gas) (Found: C, 66·9; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6%).

γ-(6-Methoxy-1-naphthyl)butyric acid (I) was obtained by heating the malonic acid at 190° until liberation of carbon dioxide ceased. It crystallised from aqueous alcohol in colourless flat needles, m. p. 150—151° (Found: C, 73·9; H, 6·65; equiv., 240·5. Calc. for $C_{15}H_{16}O_3$: C, 73·7; H, 6·6%; equiv., 244). Butenandt and Schramm (*Ber.*, 1935, **68**, 2089) obtained this acid in poor yield by another method. The *ethyl* ester was prepared with alcoholic hydrogen chloride, and formed a colourless liquid (7·8 g.), b. p. 169°/0·2 mm. (Found: C, 74·8; H, 7·5. $C_{17}H_{20}O_3$ requires C, 74·9; H, 7·4%). When this ester (0·55 g.) was heated on the water-bath for an hour with 80% sulphuric acid (3 c.c.), it gave the 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene described by Butenandt and Schramm (*loc. cit.*) together with a little of the corresponding hydroxy-ketone.

Condensation of Ethyl γ-(6-*Methoxy*-1-*naphthyl)butyrate with Ethyl Oxalate*.—Potassium (0·92 g.) was dissolved in a mixture of anhydrous ether (31·5 c.c.) and absolute alcohol (3·5 c.c.), and the suspension was cooled in ice and treated with ethyl oxalate (5 g.), and then, after ½ hour, with ethyl methoxynaphthylbutyrate (6·25 g.). At the end of a further ½ hour, the yellow solution began to deposit crystals of a potassio-compound of the condensation product. After being kept at room temperature over-night, these were collected, washed with anhydrous ether, and decomposed with ice-cold dilute sulphuric acid. The oxalyl ester was dried in ethereal solution, and the ether removed, leaving a yellow viscous liquid (6·25 g.).

7-*Methoxy*-3 : 4-*dihydrophenanthrene*-1 : 2-*dicarboxylic Anhydride*.—The foregoing oxalyl ester (1 g.), warmed on the water-bath for 5 minutes with 80% sulphuric acid (8·5 c.c.), became converted into an orange solid. This was collected, washed, and dried. 7-*Methoxy*-3 : 4-*dihydrophenanthrene*-1 : 2-*dicarboxylic anhydride* crystallised from acetic acid or benzene in orange needles, m. p. 217·5—218·5°; benzene solutions had a strong green fluorescence (Found: C, 73·1; H, 4·3. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·3%). Demethylation to 7-*hydroxy*-3 : 4-*dihydrophenanthrene*-1 : 2-*dicarboxylic anhydride* was effected by boiling a suspension of the anhydride (1 g.) in acetic acid (25 c.c.) and hydrobromic acid (*d* 1·48; 10 c.c.) for 3 hours (a clear solution was formed after 1½ hours). The solution was concentrated on the water-bath under reduced pressure, and the residue extracted with hot benzene and then recrystallised from acetic acid (0·7 g. of chocolate-brown prisms). After several recrystallisations from dioxan the hydroxy-anhydride formed golden-yellow prismatic needles, m. p. 275—278° after sintering (the colour rapidly changes to red on heating) (Found: C, 71·3; H, 3·5. $C_{16}H_{10}O_4$ requires C, 72·2; H, 3·8%).

7-*Methoxyphenanthrene*-1 : 2-*dicarboxylic Anhydride* (II).—The dihydro-compound (0·1 g.) was heated at 300° for 1½ hours with platinum-black (50 mg.), and the product was sublimed under reduced pressure. The *methoxy-anhydride* (II) crystallised from glacial acetic acid in fine yellow needles, m. p. 253—254° (260—261°, corr.) (Found: C, 73·2; H, 3·7. $C_{17}H_{10}O_4$ requires C, 73·35; H, 3·9%).

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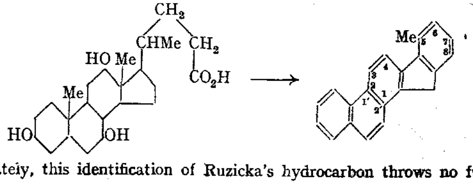
14. *The Synthesis of Compounds related to the Sterols, Bile Acids, and Oestrus-producing Hormones. Part X. Ruzicka's Hydrocarbon "$C_{21}H_{16}$" from Cholic Acid.*

By W. E. Bachmann, J. W. Cook, C. L. Hewett, and John Iball.

From the complex mixture of hydrocarbons formed by the selenium dehydrogenation of cholic acid at various temperatures Ruzicka and his collaborators (*Helv. Chim. Acta*, 1933, **16**, 216, 812; 1934, **17**, 200) have isolated 3'-methyl-1 : 2-*cyclo*pentenophenanthrene, chrysene, picene, and a hydrocarbon, m. p. 274° (corr.), to which the formula $C_{21}H_{16}$ has been ascribed. From a spectroscopic comparison of the homologous hydrocarbon "$C_{25}H_{24}$" from cholesterol with synthetic specimens of 2' : 1'-naphtha-1 : 2-fluorene and 1' : 2'-naphtha-2 : 3-fluorene, we suggested (J., 1935, 1319) that the hydrocarbon "$C_{21}H_{16}$" from cholic acid is a methyl derivative of 2' : 1'-naphtha-1 : 2-fluorene. This corresponds with the formula $C_{22}H_{16}$, which accords with the *X*-ray crystallographic evidence of Bernal and Crowfoot (J., 1935, 98) that the hydrocarbon contains 22 rather than 21 carbon atoms in the molecule. It is easy to devise possible dehydrogenation-mechanisms which might lead to a methylnaphthafluorene with the methyl group at one of the positions 4, 5, 6, 7, and 8. Accordingly, we have undertaken the synthesis of all five of these methylnaphthafluorenes. Of these, the 5-methyl compound had m. p. 275—276° (corr.) and the 8-methyl compound had m. p. 281—281·5° (corr.). The other three synthetic hydrocarbons had m. p.'s so far removed from that of the cholic acid hydrocarbon that they could be excluded on this ground alone. 8-*Methyl*-2' : 1'-*naphtha*-1 : 2-*fluorene* crystallised in two forms; the unit cell dimensions of the orthorhombic modification were different from the values for Ruzicka's hydrocarbon quoted by Bernal and Crowfoot (*loc. cit.*) (see table on p. 56) and hence there remained for consideration only the 5-methyl compound.

Through the kindness of Professor Ruzicka, who generously placed at our disposal his whole stock of the hydrocarbon from cholic acid, we have been able to compare his compound with our synthetic 5-*methyl*-2' : 1'-*naphtha*-1 : 2-*fluorene*. On account of the very small quantity of pure hydrocarbon available, the comparison has not been so complete as we would have wished, but the results completely support the view that the two compounds are identical. The m. p.'s of the two hydrocarbons (synthetic and from cholic acid) correspond within a few degrees, and the mixed m. p. shows no depression. This is not of great significance, however, as the 2'- and 3'-methylnaphthafluorenes and also the parent hydrocarbons have very similar m. p.'s (about 330°) which are not depressed by mixing. But all of the synthetic naphthafluorene hydrocarbons which we have examined are oxidised to characteristic yellow or orange ketones which give intense permanganate-like colours with concentrated sulphuric acid, and although the m. p.'s of several of these ketones lie close together, mixed m. p.'s show large depressions. By oxidation of an impure specimen of the cholic acid hydrocarbon we obtained a crude ketone, which after purification corresponded completely in its properties with synthetic 5-*methyl*-2' : 1'-*naphtha*-1 : 2-*fluorenone*, and the mixed m. p. showed no depression.

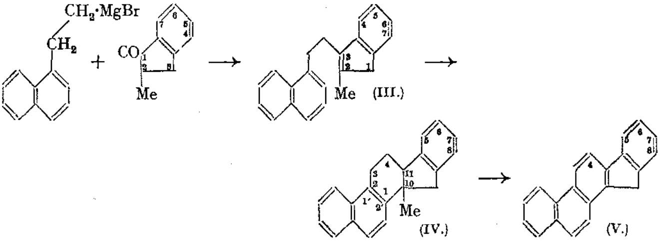
The formation of the hydrocarbon (II) from cholic acid (I) is thus due to simple cyclisation of the side chain during dehydrogenation, with elimination of oxygen from a hypothetical intermediate ketone :

(I.)  (II.)

Unfortunately, this identification of Ruzicka's hydrocarbon throws no further light

on the structure of the pentacyclic hydrocarbons of analogous structure obtained by dehydrogenation of sterols, for if a similar mechanism prevailed, cholesterol should give 5-methyl-8-*iso*propyl-2′ : 1′-naphtha-1 : 2-fluorene, which has been synthesised and is different from the cholesterol hydrocarbon (Cook, Hewett, Mayneord, and Roe, J., 1934, 1727). We regard it as certain, however, that these hydrocarbons from sterols are derived from 2′ : 1′-naphtha-1 : 2-fluorene.

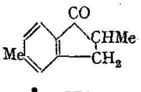
The method used for the synthesis of the new homologues of 2′ : 1′-naphtha-1 : 2-fluorene is essentially that employed for the parent hydrocarbon (Cook, Hewett, Mayneord, and Roe, *loc. cit.*). It was found that the influence of the methyl group (III) in promoting cyclisation to the desired polycyclic structure was so great that the use of β-5-tetralylethyl alcohol as a starting point in the synthesis was unnecessary. The more easily accessible β-1-naphthylethyl alcohol was employed in all cases, and no difficulties were encountered due to spiran formation by *peri*-cyclisation in the naphthalene system. The following scheme represents the course of the synthesis, 2-methylhydrindone and three dimethyl compounds being obtained through the malonic acids arising from condensation of benzyl chloride and the three xylyl bromides, respectively, with ethyl methylmalonate :



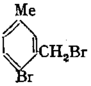
(III.) (IV.) (V.)

For the synthesis of *4-methyl-2′ : 1′-naphtha-1 : 2-fluorene*, the β-1-naphthylethyl alcohol was replaced by α-1-*naphthyl*iso*propyl alcohol*, obtained from 1-naphthylmagnesium bromide and propylene oxide. The Grignard condensation of the corresponding *naphthyl*-iso*propyl chloride* with 2-methylhydrindone gave unsatisfactory results, the desired product being obtained in poor yield, contaminated with αδ-*di*-1-*naphthyl*-βγ-*dimethylbutane*, but this was removed in a subsequent stage, and a small quantity of the pure 4-methylnaphthafluorene was isolated.

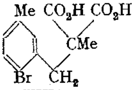
The hydrindone obtained from *m*-xylyl bromide was apparently homogeneous, and evidently had the structure (VI), formed by cyclisation in the *p*-, and not the *o*-position with respect to the methyl group, for the final 7-methylnaphthafluorene was different from 5-methylnaphthafluorene, which would be the product of *o*-ring-closure of the substituted phenylpropionic acid.



(VI.)

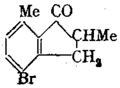


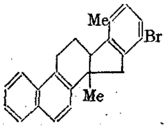
(VII.)



(VIII.)

(IX.)





(X.)

In order to obtain 5-methyl-2′ : 1′-naphtha-1 : 2-fluorene this *o*-ring-closure was brought about by blocking the *p*-position. For this purpose, ethyl methylmalonate was condensed with the mixture of chloromethyl compounds obtained by chloromethylation of *p*-bromotoluene (Fieser and Seligman, *J. Amer. Chem. Soc.*, **1935**, **57**, **942**). From the resulting mixture of substituted malonic acids, *2-bromo-5-methylbenzylmethylmalonic acid* (VIII) was isolated. The same acid was obtained from the mono-bromination product (evidently mainly VII) of *m*-xylyl bromide, and the fact that the same acid was formed from both *p*-bromotoluene and *m*-xylyl bromide is conclusive proof of its structure, from which it follows that the substituted hydrindone prepared from this acid must have structure (IX). Grignard condensation with this hydrindone, and cyclisation of the indene proceeded normally, the resulting pentacyclic *bromo*-compound (X) being debrominated by catalytic hydrogenation before dehydrogenation. This was not essential, however, as 5-methyl-2′ : 1′-naphtha-1 : 2-fluorene (II) was obtained directly from (X) by selenium dehydrogenation.

Crystal Structure of 5- *and* 8-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorenes*.—8-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene*. Two kinds of crystals were obtained by crystallisation from amyl acetate: (*a*) white ill-bounded plates of moderate size, which proved to be monoclinic; and (*b*) a few extremely thin transparent plates elongated in one direction (*b* axis); these were orthorhombic. The orthorhombic form has a large unit cell, and the table shows that the dimensions are sufficiently different from those of Ruzicka's hydrocarbon for there to be no doubt that the two compounds are different. The halvings observed on moving-film photographs suggest that the space group is $C_{2v}^{16} - B\ mam$.

The monoclinic variety has a unit cell one-fourth the size of the orthorhombic cell. The cell chosen has a β-angle of almost 90°, but the cell is genuinely monoclinic, as is shown by the moving-film photographs about the symmetry axis (*b*). The intensity of the (*h0l*) planes is widely different from that of the ($h0\bar{l}$) planes. The only halvings observed are the (0*k*0) planes when *k* is odd. Two space groups are available, *viz.*, $C_2^2 - P2_1$, and $C_{2h}^2 - P2_1/m$. As it is impossible from its chemical structure for this compound to possess the plane or centre of symmetry required by the space group C_{2h}^2 with only two molecules in the cell, it is probable that the space group is $C_2^2 - P2_1$.

5-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene*. The crystals of this compound, though also very thin plates, were better developed than those of either form of the 8-methyl derivative. The crystals show positive birefringence, the optic axial plane being (010) with *b* = β and γ slightly inclined to the perpendicular to (001). The halvings observed suggest the space group $C_{2h}^5 - P2_1/a$, but, as the unit cell has only two molecules, this would imply that each molecule possesses a centre of symmetry. This is not possible from the chemical formula, so it is probable either that the halvings (*h0l*) when *h* is odd are accidental, or that the halvings (0*k*0) when *k* is odd are accidental. In the former case the space group would be $C_2^2 - P2_1$ and in the latter $C_s^2 - Pa$. It is of interest that in the case of the monoclinic variety of the 8-methyl compound, only a few planes were observed having indices (*h0l*) when *h* is odd, and all these gave very weak reflections.

Table of Unit Cell Dimensions.

Compound.	*a.*	*b.*	*c.*	*β.*	Probable space group.
8-Methyl-2′ : 1′-naphtha-1 : 2-fluorene (orthorhombic)	17·54 Å.	5·88 Å.	27·8 Å.	90°	*B mam*
8-Methyl-2′ : 1′-naphtha-1 : 2-fluorene (monoclinic) ...	8·17	6·68	13·67	90·5	$P2_1$
5-Methyl-2′ : 1′-naphtha-1 : 2-fluorene (monoclinic) ...	9·53	5·78	13·37	92·5	*Pa* or $P2_1$
Ruzicka's hydrocarbon * (orthorhombic)	8·70	6·41	27·2	90	*Aba*

* Quoted from Bernal and Crowfoot (*loc. cit.*).

Comparison between Ruzicka's Hydrocarbon and 5-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene*.—The crystals obtained for the 5-methyl compound were monoclinic and therefore it is impossible to compare the unit cell dimensions of these crystals with those given by Bernal and Crowfoot for Ruzicka's hydrocarbon which has an orthorhombic cell. Since there was not sufficient of the purest sample of Ruzicka's compound for recrystallisation, no attempt could be made to obtain a monoclinic variety. Impure samples gave crystals

much too small for any measurements to be made. However, by the melting of a small quantity of the purest sample and of the synthetic 5-methyl-2′ : 1′-naphtha-1 : 2-fluorene in Lindemann glass capillary tubes under identical conditions, specimens which gave almost identical powder photographs were obtained. A comparison between powder photographs of the synthetic compound taken before and after melting showed clearly that this substance did not crystallise from the melt in the monoclinic form previously obtained from solution. When the powder photographs of each specimen produced from the melt were superimposed, the rings appeared exactly to coincide, the relative intensity of the rings being also apparently the same in each case. Careful measurement of the rings showed, however, that there was a slight difference between the diameters of the outer rings. The difference was slightly greater than the maximum error of measurement, but in no case did the difference between the diameters of corresponding rings represent a difference in spacing of more than 1%. It is possible that this difference may be caused by traces of impurities in Ruzicka's hydrocarbon, as this did not melt so sharply as the synthetic compound.

The conclusion from these facts is that the synthetic compound, though normally crystallising in a monoclinic form, can crystallise in some other form, presumably orthorhombic. There is nothing in the crystal structure data inconsistent with the identity of the two samples; in fact, the similarity between the powder photographs is sufficiently close to make it highly probable that they do consist of the same substance.

EXPERIMENTAL.

Preparation of Hydrindones.—A solution of β-tolyl-α-methylpropionyl chloride (1 part) in ligroin (b. p. 80—100°; 1·5 parts) was added drop by drop to a suspension of powdered anhydrous aluminium chloride (1 part) in ligroin (1 part) with continuous shaking (compare Ingold and Piggott, J., 1923, **123**, 1502); the mixture was then heated gradually to the boiling point. The hydrindone obtained on hydrolysis of the mixture was purified by vacuum distillation.

Dehydration of Carbinols to Indenes.—The crude carbinols (1 part) obtained from the Grignard reaction between the hydrindones and β-1-naphthylethylmagnesium bromide were heated with potassium hydrogen sulphate (1·5 parts) at 160° for 1 hour. The mixture was treated with water and the indene was purified by crystallisation or distillation.

Cyclisation of Indenes.—A mixture of the indene (1 part), carbon disulphide (10 parts), and anhydrous aluminium chloride (1 part) was kept at 0° for 3 hours with occasional shaking. The solution was decanted from the sludge into water and the product was isolated from the solution by vacuum distillation.

Dehydrogenation.—The cyclised product (1 part) was heated with selenium (1 part) at 310° for 7 hours; if heated for 20 hours, the compounds were nsually completely decomposed. The naphthafluorene hydrocarbons were recrystallised from xylene, and separated from traces of selenium by sublimation at 0·1 mm.; the selenium sublimed at 180—200°, and the hydrocarbon at 230—240°. The compounds were then recrystallised from xylene.

2′ : 1′-*Naphtha*-1 : 2-*fluorene*.—3-(β-1′-*Naphthylethyl*)-2-*methylindene* (III). A solution of 2-methyl-1-hydrindone (10 g.) in anhydrous ether (10 c.c.) was added drop by drop to an ice-cold Grignard reagent prepared from β-1-naphthylethyl bromide (24 g.) in anhydrous ether (60 c.c.). After the solution had been kept in a refrigerator for 12 hours a large amount of crystalline addition compound (A) was present; the crystals were collected and hydrolysed with ice-cold ammonium chloride solution separately from the solution (B). The indene resulting from the dehydration of the liquid carbinol obtained from the crystals (A) was recrystallised twice from benzene–alcohol; 3-(β-1′-*naphthylethyl*)-2-*methylindene* formed colourless diamond-shaped plates* (8·2 g.), m. p. 99—99·5° (Found: C, 92·7; H, 7·15. $C_{22}H_{20}$ requires C, 92·9; H, 7·1%). An additional quantity of the indene, bringing the total yield to 63%, was obtained from the carbinol formed by hydrolysis of solution B; this crude indene was distilled in a vacuum and purified through its picrate. The *dipicrate* of the indene crystallised from benzene in orange needles, m. p. 161—161·5° (Found: C, 55·1; H, 3·5. $C_{22}H_{20},2C_6H_3O_7N_3$ requires C, 55·0; H, 3·5%).

10-*Methyl*-3 : 4 : 10 : 11-*tetrahydro*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (IV). Vacuum distillation of the cyclised product from the indene (3·5 g.) gave a glassy mass (2·7 g.), b. p. 190—195°/0·2 mm. A solution of this in benzene–alcohol deposited colourless needles (0·95 g.) of 10-*methyl*-

3 : 4 : 10 : 11-*tetrahydro*-2′ : 1′-*naphtha*-1 : 2-*fluorene*, m. p. 111—112° after recrystallisation from benzene-alcohol (Found : C, 92·85; H, 7·4. $C_{22}H_{20}$ requires C, 92·9; H, 7·1%).

2′ : 1′-*Naphtha*-1 : 2-*fluorene*. This was obtained in 90% yield * by dehydrogenation of the crystalline methyltetrahydro-derivative; it had m. p. 328° and was identical with that obtained by the use of β-5-tetralylethyl chloride (Cook, Hewett, Mayneord, and Roe, J., 1934, 1737). A further quantity of naphthafluorene was obtained by dehydrogenation of the mother-liquors of the cyclised product, the total yield being 34% with respect to the indene.

6-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene*.—2 : 6-*Dimethylhydrindone*. *p*-Xylyl bromide (28 g.) was condensed with the sodio-derivative of ethyl methylmalonate (32 g.) in absolute alcohol (70 c.c.) and yielded ethyl *p*-methylbenzylmethylmalonate, which was purified by distillation, b. p. 203—210°/26 mm. This ester (23 g.) was hydrolysed to p-*methylbenzylmethylmalonic acid* (18 g.); a sample of the acid crystallised from benzene in colourless needles, m. p. 178—180° with evolution of carbon dioxide (Found : C, 64·7; H, 6·4. $C_{12}H_{14}O_4$ requires C, 64·7; H, 6·35%). The substituted malonic acid was converted into β-p-*tolyl*-α-*methylpropionic acid* by heating at 180°, and this acid distilled, b. p. 181—182°/23 mm. (yield, 90%). For analysis, a sample was recrystallised from light petroleum, forming colourless needles, m. p. 30—31·5° (Found : C, 73·7; H, 8·0. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%). A mixture of the acid (11 g.) and thionyl chloride (15 c.c.) was refluxed for 2 hours and the resulting acid chloride was purified by distillation (b. p. 139—140°/21 mm.; yield, 98%).

2 : 6-Dimethylhydrindone, b. p. 145—148°/21 mm., was obtained in 97% yield from the foregoing acid chloride. It was analysed in the form of its crystalline *phenylhydrazone*, which formed long cream-coloured needles from benzene-alcohol, m. p. 173—175° (decomp.) (Found : C, 81·5; H, 7·6. $C_{17}H_{18}N_2$ requires C, 81·6; H, 7·3%).

3-(β-1′-*Naphthylethyl*)-2 : 5-*dimethylindene*. 2 : 6-Dimethylhydrindone (8 g.) in anhydrous ether (8 c.c.) was added to the ice-cold Grignard reagent from β-1-naphthylethyl bromide (18 g.); the mixture soon deposited crystals of the addition product. The indene obtained from the carbinol isolated from the crystalline portion crystallised readily; the indene from the mother-liquors was purified through its picrate; total yield, 7·7 g. or 51%. 3-(β-1′-*Naphthylethyl*)-2 : 5-*dimethylindene* crystallised from benzene-alcohol in colourless rectangular plates, m. p. 81—81·5° (Found : C, 92·3; H, 7·4. $C_{23}H_{22}$ requires C, 92·6; H, 7·4%). The *dipicrate* crystallised from benzene in orange needles, m. p. 144—144·5° (Found : N, 11·3. $C_{23}H_{22},2C_6H_3O_7N_3$ requires N, 11·1%).

6 : 10-*Dimethyl*-3 : 4 : 10 : 11-*tetrahydro*-2′ : 1′-*naphtha*-1 : 2-*fluorene*. Vacuum distillation of the cyclised product from the aforesaid indene (5·3 g.) gave a gum (4 g.), b. p. 190—200°/0·1 mm.; an alcohol-acetone solution of this product after 2 days in a refrigerator deposited fine colourless needles of 6 : 10-*dimethyl*-3 : 4 : 10 : 11-*tetrahydro*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (1 g.), m. p. 106·5—107° after recrystallisation from acetone-alcohol (Found : C, 92·7; H, 7·4. $C_{23}H_{22}$ requires C, 92·6; H, 7·4%). The *semipicrate* crystallised from benzene in stout needles, m. p. 133·5—134° (Found : N, 5·6. $2C_{23}H_{22},C_6H_3O_7N_3$ requires N, 5·4%).

6-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene*. Dehydrogenation of the crystalline dimethyltetrahydronaphthafluorene gave a 70% yield of the methylnaphthafluorene; the compound can also be obtained conveniently by dehydrogenation of the crude cyclisation product. 6-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene* crystallised from xylene in colourless leaflets, m. p. 330°,† in a bath preheated to 300° (Found : C, 94·2; H, 5·9. $C_{22}H_{16}$ requires C, 94·2; H, 5·8%). The total yield of 6-methylnaphthafluorene based on the indene was 30%. Oxidation of the hydrocarbon (0·1 g.) by 1 hour's heating with potassium dichromate (0·3 g.) in acetic acid (5 c.c.) gave a 60% yield of 6-*methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorenone*; the ketone after sublimation at 230°/0·1 mm. was obtained in fine golden-yellow needles, m. p. 225—226°, by recrystallisation from acetic acid (Found : C, 89·7; H, 4·9. $C_{22}H_{14}O$ requires C, 89·8; H, 4·8%). Like the parent naphthafluorenone, this and all the other methylnaphthafluorenones give with concentrated sulphuric acid an intense purple colour which changes gradually to magenta. This ketone depressed the m. p. of 2′ : 1′-naphtha-1 : 2-fluorenone.

* As Edisburg, Morton, and Lovern (*Biochem. J.*, 1935, **29**, 907) have recently remarked on "the well-known inefficiency of the selenium dehydrogenation process (order of yield 3—10%)," it seems necessary to add that in our hands this process has given consistently good yields (50—90%) with simple polycyclic hydroaromatic compounds. For a discussion of special cases which do not give good results by this method, see J., 1934, 1734; following paper.

† The m. p.'s of the three naphthafluorene hydrocarbons having m. p.'s above 300° were very much influenced by the rate of heating, on account of decomposition.

7-Methyl-2′ : 1′-naphtha-1 : 2-fluorene.—2 : *5-Dimethylhydrindone* (VI). The ester (30 g., b. p. 185—188°/21 mm.) resulting from the condensation of *m*-xylyl bromide (37 g.) with the sodio-derivative of ethyl methylmalonate (40 g.) was hydrolysed to m-*methylbenzylmethylmalonic acid* (19 g.); this acid crystallised from benzene in colourless needles, m. p. 152—153°, with liberation of carbon dioxide (Found: C, 64·6; H, 6·4. $C_{12}H_{14}O_4$ requires C, 64·7; H, 6·35%). At 180° the substituted malonic acid (18 g.) was decarboxylated to β-m-*tolyl-α-methylpropionic acid*, which was purified by distillation, b. p. 178—179°/20 mm.; yield, 97% (Found: C, 73·4; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%). This acid was converted into its chloride (97% yield), b. p. 137—138°/21 mm., which was then cyclised to 2 : *5-dimethylhydrindone* (80% yield), b. p. 142—144°/21 mm. (Found: C, 81·5; H, 7·7. $C_{11}H_{12}O$ requires C, 82·5; H, 7·6%). The 2 : *4-dinitrophenylhydrazone* of the hydrindone crystallised from chloroform in scarlet needles, m. p. 225—226° (decomp.) (Found: N, 16·6. $C_{17}H_{16}O_4N_4$ requires N, 16·5%).

3-(β-1′-*Naphthylethyl*)-2 : *6-dimethylindene.* The liquid carbinol which was obtained by interaction of 2 : 5-dimethylhydrindone (7 g.) with the Grignard reagent from β-1-naphthylethyl bromide (16 g.) was dehydrated to the indene; after two conversions into the picrate, followed by vacuum distillation of the regenerated hydrocarbon, 3-(β-1′-*naphthylethyl*)-2 : 6-*dimethylindene* (6 g.) was obtained as an extremely viscous, yellowish liquid, b. p. 184—186°/0·05 mm. (Found: C, 92·2; H, 7·4. $C_{23}H_{22}$ requires C, 92·6; H, 7·4%).

7-Methyl-2′ : 1′-naphtha-1 : 2-fluorene. The distilled cyclisation product (3·2 g.), b. p. 195—198°/0·15 mm., from the indene (4·5 g.) formed a glassy mass; a solution of the product in acetone–alcohol deposited colourless prisms (0·5 g.), m. p. 101°, which proved to be αδ-di-1-naphthylbutane, undoubtedly present in the indene as an impurity carried through from the Grignard reaction (Found: C, 93·0; H, 7·0. Calc.: C, 92·85; H, 7·15%). The compound was identical with a sample prepared by interaction of β-1-naphthylethyl bromide and magnesium. The melting points of its yellow *dipicrate*, m. p. 174—175° (Found: N, 11·2. $C_{24}H_{22},2C_6H_3O_7N_3$ requires N, 11·0%) and *s*-trinitrobenzene complex, m. p. 186·5°, were in agreement with Harper, Kon, and Ruzicka (J., 1934, 124). After removal of the dinaphthylbutane, the mother-liquor deposited 7 : 10-*dimethyl*-3 : 4 : 10 : 11-*tetrahydro*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (0·2 g.), which crystallised from alcohol–acetone in colourless triangular prisms, m. p. 134·5—135° (Found: C, 92·9; H, 7·1. $C_{23}H_{22}$ requires C, 92·6; H, 7·4%). Dehydrogenation of the crystals gave *7-methyl-2′ : 1′-naphtha-1 : 2-fluorene*; after purification this compound formed colourless leaflets, m. p. 334—336° in a bath preheated to 300° (Found: C, 94·4; H, 5·8. $C_{22}H_{16}$ requires C, 94·2; H, 5·8%). Dehydrogenation of the cyclisation product without isolation of the crystalline intermediate gave 7-methylnaphthafluorene in 25% yield; in this case the methylnaphthafluorene which was formed after 7 hours was removed, and the oil again subjected to the action of selenium for two like periods. *7-Methyl-2′ : 1′-naphtha-1 : 2-fluorenone*, obtained from the hydrocarbon by oxidation with potassium dichromate in acetic acid, formed golden-yellow needles, m. p. 175—176·5°, from acetic acid, after vacuum sublimation (Found: C, 89·7; H, 4·9. $C_{22}H_{14}O$ requires C, 89·8; H, 4·8%).

8-Methyl-2′ : 1′-naphtha-1 : 2-fluorene.—2 : *4-Dimethylhydrindone*? Hydrolysis of the ester (31·5 g., b. p. 184—190°/21 mm.) which was obtained by the condensation of *o*-xylyl bromide (43 g.) with the sodio-derivative of ethyl methylmalonate (40 g.) gave o-*methylbenzylmethylmalonic acid* (21 g.); this acid crystallised from benzene–light petroleum in clusters of colourless needles, m. p. 122·5—123° (Found: C, 64·5; H, 6·45. $C_{12}H_{14}O_4$ requires C, 64·7; H, 6·35%). Decarboxylation of the substituted malonic acid at 180° gave a 93% yield of β-o-*tolyl-α-methylpropionic acid*, b. p. 179—180°/20 mm. (Found: C, 74·1; H, 8·1. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%). The acid chloride, b. p. 137—138°/21 mm., prepared in 93% yield by the action of thionyl chloride, was cyclised to 2 : *4-dimethylhydrindone* (90% yield), a yellowish liquid, b. p. 147—149°/20 mm., which was not obtained analytically pure (Found: C, 81·4; H, 7·7. $C_{11}H_{12}O$ requires C, 82·5; H, 7·25%). The *semicarbazone* formed colourless needles (from dioxan), m. p. 224—225° (decomp.) (Found: N, 19·5. $C_{12}H_{15}ON_3$ requires N, 19·4%).

8-Methyl-2′ : 1′-naphtha-1 : 2-fluorene. Dehydration of the carbinol resulting from interaction of 2 : 4-dimethylhydrindone (9 g.) with the Grignard reagent from β-1-naphthylethyl bromide (21 g.) in anhydrous ether (60 c.c.) gave the indene; after two recrystallisations from benzene–alcohol 3-(β-1′-*naphthylethyl*)-2 : 7-*dimethylindene* formed colourless plates, m. p. 96°; the melt quickly solidified and remelted at 113·5—114° (Found: C, 92·1; H, 7·4. $C_{23}H_{22}$ requires C, 92·6; H, 7·4%). Vacuum distillation of the cyclisation product of the indene (8·9 g.) gave a viscous oil (7·2 g.), b. p. 195—200°/0·2 mm.; crystals of 8 : 10-*dimethyl*-3 : 4 : 10 : 11-*tetrahydro*-2′ : 1′-*naphtha*-1 : 2-*fluorene* (1·7 g.) separated from an alcohol–acetone

solution of the product; this crystallised from acetone in colourless rectangular plates, m. p. 121—122° (Found: C, 92·55; H, 7·4. $C_{23}H_{22}$ requires C, 92·6; H, 7·4%). The *semipicrate* crystallised from absolute alcohol in broad crimson needles, m. p. 130·5—131·5° (Found: C, 75·3; H, 5·8. $2C_{23}H_{22},C_6H_3O_7N_3$ requires C, 75·6; H, 5·7%). Two 7-hour treatments with selenium gave a 98% yield of *8-methyl-2′ : 1′-naphtha-1 : 2-fluorene*, which after the usual purification crystallised from xylene in broad colourless needles, or leaflets, m. p. 272·5—273° (281—281·5° corr.) (Found: C, 94·5; H, 5·5. $C_{22}H_{16}$ requires C, 94·2; H, 5·8%); the total yield of the hydrocarbon, including that obtained from the mother-liquors, was 27% based on the indene. Oxidation yielded *8-methyl-2′ : 1′-naphtha-1 : 2-fluorenone* (70% yield), which crystallised from acetic acid in fine golden-yellow needles, m. p. 237—238° (Found: C, 89·8; H, 5·0. $C_{22}H_{14}O$ requires C, 89·8; H, 4·8%).

5-Methyl-2′ : 1′-naphtha-1 : 2-fluorene.—7-Bromo-3-(β-1′-naphthylethyl)-2 : 4-dimethylindene. A mixture of 2- and 3-chloromethyl-4-bromotoluenes (Fieser and Seligman, *loc. cit.*) was added gradually to the sodio-derivative of ethyl methylmalonate (40 g.) in absolute alcohol (90 c.c.); after 1½ hours' refluxing, the mixture was treated with water, and the resulting ester purified by vacuum distillation (b. p. 135—138°/0·05 mm.; yield, 48 g.). Hydrolysis of the ester was accomplished by ½ hour's heating with a solution of potassium hydroxide (70 g.) in methyl alcohol (70 c.c.) and water (70 c.c.); acidification yielded a mixture of the malonic acids (37 g.). In one experiment this mixture was used in the subsequent steps and gave a satisfactory yield of the desired indene. In another experiment the mixture was subjected to repeated recrystallisations from benzene–methyl alcohol (6 : 1) and 4·5 g. of pure *2-bromo-5-methylbenzylmethylmalonic acid* (VIII), the less soluble isomeride, were obtained as large colourless plates, m. p. 179—180° with liberation of carbon dioxide (Found: C, 48·3; H, 4·6. $C_{12}H_{13}O_4Br$ requires C, 47·8; H, 4·35%). The structure of this compound was proved by its synthesis from *m*-xylyl bromide; the latter compound (15 g.) was treated with bromine (13 g.) at 0° in presence of iron powder; the purified product (mostly VII) (6·5 g., b. p. 148—152°) was condensed with ethyl sodiomethylmalonate and the resulting ester on hydrolysis yielded 2-bromo-5-methylbenzylmethylmalonic acid (2·2 g.), m. p. 179—180°, identical with the malonic acid obtained as described above. Decarboxylation of the substituted malonic acid at 180° gave *α-2-bromo-5-methylbenzylpropionic acid* in 90% yield; this acid formed colourless plates, m. p. 84—85°, from light petroleum (Found: C, 51·8; H, 5·4. $C_{11}H_{13}O_2Br$ requires C, 51·4; H, 5·1%). Cyclisation of the acid chloride, b. p. 173—174°/20 mm., obtained from the acid in 97% yield, gave an 86% yield of 4-bromo-2 : 7-dimethylhydrindone (IX), which formed a yellowish liquid, b. p. 115—117°/0·15 mm.

Dehydration of the carbinol resulting from interaction of the hydrindone with β-1-naphthylethylmagnesium bromide gave a 41% yield of *7-bromo-3-(β-1′-naphthylethyl)-2 : 4-dimethylindene*, which crystallised from benzene–alcohol in colourless needles, m. p. 84—85° (Found: C, 73·3; H, 5·8. $C_{23}H_{21}Br$ requires C, 73·2; H, 5·6%). The *dipicrate* crystallised from benzene in clusters of fine orange needles, m. p. 142·5—143·5° (Found: C, 50·7; H, 3·4. $C_{23}H_{21}Br,2C_6H_3O_7N_3$ requires C, 50·3; H, 3·3%).

5-Methyl-2′ : 1′-naphtha-1 : 2-fluorene. The indene (3 g.) was cyclised and the product was taken up in benzene–alcohol; after several hours the solution deposited crystals of *8-bromo-5 : 10-dimethyl-3 : 4 : 10 : 11-tetrahydro-2′ : 1′-naphtha-1 : 2-fluorene* (X) (1·57 g.). This compound, after two recrystallisations from absolute alcohol containing a trace of benzene, formed colourless plates, m. p. 137·5—138·5° (Found: C, 73·5; H, 6·0. $C_{23}H_{21}Br$ requires C, 73·2; H, 5·6%). By passing a stream of hydrogen through a boiling mixture of the aforementioned compound (1 g.) and palladium-black (0·5 g.) in acetic acid (25 c.c.) for 3 hours, the debrominated product (0·3 g.) was obtained in addition to unchanged material. Selenium dehydrogenation gave *5-methyl-2′ : 1′-naphtha-1 : 2-fluorene* (0·15 g.), which crystallised from xylene in leaflets, m. p. 275—276° (corr.) (Found: C, 94·1; H, 6·0. $C_{22}H_{16}$ requires C, 94·2; H, 5·8%); mixed with the 8-methyl isomeride, it melted at 271·5—272·5° (corr.). *5-Methyl-2′ : 1′-naphtha-1 : 2-fluorenone*, obtained in 70% yield by oxidation, crystallised from ethyl acetate in golden-yellow needles, m. p. 209—210° (Found: C, 89·3; H, 4·6. $C_{21}H_{14}O$ requires C, 89·8; H, 4·8%). The mixed m. p. with 8-methylnaphthafluorenone was 187—195°.

4-Methyl-2′ : 1′-naphtha-1 : 2-fluorene.—α-1-Naphthylisopropyl alcohol. Propylene oxide (40 g.) was added to an ice-cold Grignard solution prepared from 1-bromonaphthalene (67 c.c.), magnesium turnings (12 g.), and anhydrous ether (500 c.c.). After being kept over-night at room temperature, the ether was distilled off, and the residue heated on the water-bath for an hour. The whole was extracted with ether and ammonium chloride solution, and the ethereal extract dried (sodium sulphate) and distilled. The product (43 g.) formed a pale yellow,

viscous oil, b. p. 148—155°/25 mm. A sample for analysis was purified through the 3 : 5-*dinitrobenzoate*, which separated from ethyl acetate as a yellowish microcrystalline powder, m. p. 171—172° (Found: C, 63·25; H, 4·4. $C_{20}H_{16}O_6N_2$ requires C, 63·1; H, 4·2%). Hydrolysis with boiling alcoholic potash gave α-1-*naphthylisopropyl alcohol*, which was distilled at 0·1 mm. from an air-bath at 130—140°. It formed a colourless syrup (Found: C, 83·4; H, 7·6. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The corresponding *chloride*, formed by slow addition of the crude distilled naphthyl*iso*propyl alcohol (13·5 g.) to a mixture of phosphorus trichloride (15·5 g.) and carbon tetrachloride (35 c.c.), followed by 1 hour's heating on the water-bath, was a pale yellow liquid (7·5 g.), b. p. 131°/6 mm. (Found: C, 75·2; H, 6·0. $C_{13}H_{13}Cl$ requires C, 76·25; H, 6·4%).

4-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene*. In the Grignard condensation between naphthyl-*iso*propylmagnesium chloride and 2-methylhydrindone, better results were obtained in the presence of a molecule of ethylmagnesium bromide. An ice-cold Grignard reagent from naphthyl*iso*propyl chloride (15·3 g.), ethyl bromide (8·2 g.), magnesium turnings (5·4 g.), and anhydrous ether (100 c.c.) was treated with 2-methylhydrindone (10·5 g.), kept at 0° for ½ hour, and then boiled for 1½ hours. The product was decomposed with ice and ammonium chloride, and the ethereal solution washed, dried, and distilled. The fraction, b. p. 195—215°/0·8 mm. (5·5 g.), was cyclised with aluminium chloride (5·5 g.) in carbon disulphide (55 c.c.), the mixture being kept over-night at 2—3°. The cyclised product gave a crystalline picrate, which was decomposed, and the resulting hydrocarbon was recrystallised from benzene–alcohol until it melted constantly at 131—132°. This was not dehydrogenated by selenium and hence was *αδ-di*-1-*naphthyl*-*βγ-dimethylbutane* (Found: C, 92·4; H, 7·7; *M*, Rast method, 344. $C_{26}H_{26}$ requires C, 92·5; H, 7·5%; *M*, 338).

The liquors from which the crystalline picrate had been obtained were freed from picric acid, and the resinous hydrocarbon mixture was heated with selenium (1·4 g.) at 300—320° for 24 hours. The resulting 4-*methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene* crystallised from benzene–alcohol in colourless needles, m. p. 202—203° (Found: C, 94·3; H, 5·6. $C_{22}H_{16}$ requires C, 94·2; H, 5·8%). Oxidation of this hydrocarbon (20 mg.) gave the corresponding ketone, which, after purification, crystallised from acetic acid in light brown, slender needles, m. p. 214—215°. There was insufficient for analysis.

Comparison of Ruzicka's Hydrocarbon from Cholic Acid with 5-*Methyl*-2′ : 1′-*naphtha*-1 : 2-*fluorene*.—(a) *Mixed m. p. determination*. The purest specimen of the cholic acid hydrocarbon supplied by Professor Ruzicka had m. p. 274·5—276° (uncorr.). The m. p. of the synthetic hydrocarbon taken at the same time on the same thermometer was 269—270°, and the mixed m. p. was 271—273·5°.

(b) *Comparison of ketones*. Three specimens of the hydrocarbon from cholic acid having m. p.'s 267—275°, 270—275°, and 259—262° (uncorr.) were combined. The combined sample amounted to 70 mg., of which 50 mg. was the specimen, m. p. 259—262°. This was oxidised with potassium dichromate (0·2 g.) in boiling glacial acetic acid (3·5 c.c.). The crude oxidation product was sublimed at 180—210°/0·05 mm., and then recrystallised five times from acetic acid, benzene, and ethyl acetate. The ketone then formed golden-orange needles, m. p. 207—208°, and the mixed m. p. with 5-methyl-2′ : 1′-naphtha-1 : 2-fluorenone (m. p. 209—210°) was 207·5—208·5°. The mixed m. p. with 2′ : 1′-naphtha-1 : 2-fluorenone (m. p. 207—208°) was about 180°. This specimen of the ketone prepared from Ruzicka's hydrocarbon gave the usual naphthafluorenone colour reaction with concentrated sulphuric acid.

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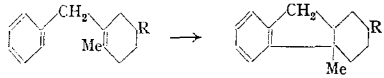
15. *The Dehydration of Benzylcyclohexanols.*

By J. W. Cook and C. L. Hewett.

In our preliminary survey of the synthesis of polycyclic hydroaromatic compounds by cyclisation of unsaturated compounds of suitable structure (J., 1933, 1098) we found that 1-benzyl*cyclo*hexanol was converted by phosphoric oxide at 160° into a saturated hydrocarbon, which we suggested was hexahydrofluorene. Further investigation was clearly desirable in view of our failure to obtain fluorene by selenium dehydrogenation of this hydrocarbon. We attributed this failure to the use of too low a temperature, consequent upon the relatively low boiling point of the hydrocarbon. If our proposed structure were correct, then similar hydrofluorene hydrocarbons (II) should be obtained more readily by cyclisation of the intermediate unsaturated hydrocarbons (I; R = H or Pr^{β}) resulting from dehydration of the *carbinols* obtained from benzylmagnesium chloride and 2-methyl*cyclo*hexanone or tetrahydrocarvone (for a discussion of the influence of a methyl group in promoting cyclisation see J., 1934, 653, 1727).

(I.)  (II.)

In agreement with this view, both hydrocarbons (I; R = H and Pr^{β}) were converted in good yield by aluminium chloride at 0° into saturated *isomerides*, whereas 1-benzyl-Δ^1-*cyclo*hexene is mainly polymerised. Both tricyclic hydrocarbons resisted the dehydrogenating action of selenium, and in the case of the methyl*iso*propyl compound this was certainly not due to the b. p. being too low. The methyl compound (from I; R = H) was likewise unaffected by 7 hours' treatment with palladised charcoal at 300°.

In the meantime, experiments in other directions made it difficult to assess the significance of these unsuccessful attempts to dehydrogenate the hydrocarbons in question. For instance, it was found (in collaboration with G. A. D. Haslewood and F. L. Warren) that saturated sterol derivatives (dihydrocholesterol, cholestane, and perhydrocalciferol) were not dehydrogenated by heating with selenium at 300—320° for 60 hours, and cholestane was only partly dehydrogenated at 340—350° (30 hours). Moreover, it was shown (in collaboration with A. Dansi) that 2-*benzyldecalin* was unaffected by selenium at 320—330°, although it was dehydrogenated to 2-benzylnaphthalene by platinum-black at 300°. A single double bond in the molecule destroyed this resistance to selenium dehydrogenation, for 2-*benzyloctalin*, obtained by dehydrating 2-*benzyl*-trans-2-*decalol*, gave 2-benzylnaphthalene with selenium at 300—320°. This difference in behaviour between platinum and palladium, on the one hand, and selenium and sulphur (which, unlike the noble metals, are able to bring about elimination of quaternary methyl groups), on the other hand, points to different mechanisms for the two types of dehydrogenating agents. Probably in the case of sulphur and selenium intermediate compounds are formed by combination with an unsaturated centre or an aromatic ring. If neither of these is present, dehydrogenation does not occur. An apparent exception to the generalisation that completely reduced rings are resistant to selenium dehydrogenation was recently given by Barrett, Cook, and Linstead (J., 1935, 1067), who obtained 2-methylnaphthalene from *trans*-2-methyldecalin, but these authors used a higher temperature (320—350°) than that which we normally employ (300—320°), and in any case they state that the yield was poor.

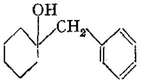
As we could not be certain that the resistance to selenium dehydrogenation shown by the tricyclic hydrocarbons from (I) was not due to the presence of the isolated *cyclo*hexane ring in (II), we decided to make a detailed study of the structure of the original tricyclic hydrocarbon from 1-benzyl*cyclo*hexanol, and also to synthesise hexahydrofluorene by an independent method. The results have shown that the dehydration product of benzyl*cyclo*hexanol is not hexahydrofluorene, but a bridged-ring compound (VII): ***hexahydro-***

fluorene, synthesised by the method described below, was smoothly dehydrogenated to fluorene by selenium at 300—320°, and was also dehydrogenated with great facility by platinum-black at 250—260°. Hence the cyclisation products of (I; R = H and Pr^{β}) cannot be hexahydrofluorene derivatives, although in the absence of further evidence we are not prepared to assert that they are homologues of (VII). It is also evident that the structure of a methyl*iso*propylhexahydrofluorene attributed by Ruzicka and Peyer (*Helv. Chim. Acta*, 1935, **18**, 678) to a hydrocarbon which they found to be unaffected by heating with selenium at 360° for 60 hours cannot be correct.

The evidence for the bridged-ring structure (VII) of the hydrocarbon from 1-benzyl*cyclo*hexanol is as follows: (a) Oxidation with dilute nitric acid at 180° gave phthalic acid, showing that in the cyclisation the alicyclic part of the molecule becomes attached at position 2 of the aromatic ring.

(b) Oxidation with cold chromic acid in acetic acid gave, in good yield, a *ketone* which formed a characteristic well-crystallised *semicarbazone* and an *oxime*. Hence the methylene group of the original benzyl group must be preserved intact. Moreover, the same ketone was formed by oxidation of the tricyclic hydrocarbon resulting from the phosphoric oxide dehydration of 1-benzyl*cyclo*hexanol (III), 2-*benzyl*cyclo*hexanol* (IV), and phenyl*cyclo*hexylcarbinol (V). The great stability of this ketone is incompatible with the spiran structure (VI), the only structure which could arise from all three carbinols without migration of a double bond in the hypothetical intermediate unsaturated hydrocarbon. The inevitable conclusion is that such a migration does occur during the cyclisation.

(c) The fact that this ketone was different from the hexahydrofluorenone synthesised from 2-phenylhexahydrobenzoic acid is fairly conclusive disproof of the hexahydrofluorene structure for the hydrocarbon from (III), (IV), and (V).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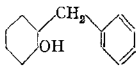
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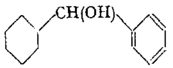
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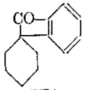
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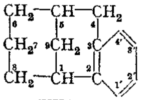
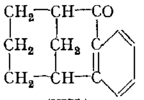
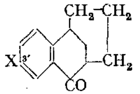

(VII.)


(VIII.)


(IX.)*

(d) The ketone (VIII) was converted by nitric acid into a crystalline *nitro*-derivative (IX; X = NO_2), in which the nitro-group evidently occupies the *m*-position with respect to the carbonyl group. This was reduced to a primary *amine* (IX; X = NH_2), which was oxidised by chromic acid to *cis*-hexahydro*iso*phthalic acid. This acid was obtained in better yield by permanganate oxidation of the *phenol* (IX; X = OH) formed by decomposition of the corresponding diazonium sulphate.

These results present some points of interest. The formation of 2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonene* (VII) by dehydration of the carbinols (III), (IV), and (V), in preference to the alternative hexahydrofluorene, is another instance of the extreme sensitivity of the course of cyclisation processes to factors of molecular environment (compare J., 1934, 653, 1727; 1935, 667, 1635). In the present instance a determining factor is probably the complete absence of strain of the *bicyclo*nonane system present in (VII); the hexahydrofluorene structure is a strained system, although not, in the *cis*-form, extensively so. A noteworthy feature is the facility with which the centre of unsaturation resulting from elimination of the hydroxyl group from the carbinols (III, IV, and V) moves round the *cyclo*hexane ring to the point necessary for the formation of the most favoured structure.

* This alternative representation of the benz*bicyclo*nonene system shows the relationship of these compounds to tetralin.

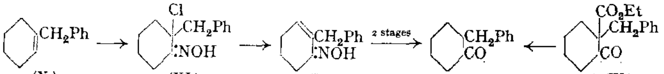
This is particularly remarkable with (V), which gave almost as good yield of (VII) as the other carbinols. The parent hydrocarbon, 1 : 3 : 3-*bicyclo*nonane, and many of its simple derivatives were prepared by Meerwein (*Annalen*, **1913**, **398**, 196; *J. pr. Chem.*, 1922, **104**, 161) and their formation and properties reflect the strainless character of this system * (for a theoretical discussion of this and other strainless polycyclic systems see Mohr, *J. pr. Chem.*, 1918, **98**, 315). In our tricyclic hydrocarbon (VII) condensation with the aromatic nucleus presumably introduces a slight strain on account of the deviation from the tetrahedral angle of the valencies of carbon atoms 2 and 3, but it is apparent from a model that any strain so introduced is inappreciable.

We could obtain no evidence of dehydrogenation of benz*bicyclo*nonene (VII) either with selenium (see above), or with platinum-black at 300°, or with platinised asbestos at 340—360°, using the technique of Ehrenstein (*Arch. Pharm.*, 1931, **269**, 648). This cannot be attributed entirely to absence of strain, for Kasansky and Plate (*Ber.*, 1935, **68**, 1259) have shown that a methyl derivative of 2 : 2 : 2-*bicyclo*octane, which also is a completely strainless system (Aschan, *Acta Soc. Sci. Fennicae*, 1896, **21**, No. 5, 124; compare Mohr, *loc. cit.*), is susceptible to the action of a dehydrogenating catalyst.

The great stability of the benz*bicyclo*nonene ring system is reflected in the properties of 2 : 3-benz-1 : 3 : 3-*bicyclo*-Δ^2-nonen-4-one (VIII). This ketone was unaffected by sodium dichromate in boiling glacial acetic acid (10 hours); with potassium permanganate in pure acetone, only the solvent was oxidised; bromine in carbon disulphide had no action in 48 hours. The last is remarkable, as the ketone appears to contain an enolisable hydrogen atom. The inactivity towards bromine may be due to suppression of enolisation on account of the reluctance of the system to assume a double bond at the position 4 : 5, although, as Hückel ("Theoretische Grundlagen der organische Chemie," 1934, I, 74) has pointed out, Bredt's rule for the camphane system is not valid for more complex systems. An attempt to methylate the ketone (VIII) with sodamide and methyl iodide gave only unchanged ketone; boiling concentrated nitric acid had no oxidising action on the ketone, but merely led to the nitro-ketone (IX; $X = NO_2$).

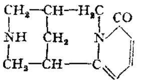
From the theoretical standpoint, the oxidation of 3′-hydroxy-2 : 3-benz-1 : 3 : 3-*bicyclo*-Δ^2-nonen-4-one to *cis*-hexahydro*iso*phthalic acid provides experimental proof of the *cis* attachment of the "bridge" carbon atom to the 1 : 5-carbon atoms of the eight-membered ring, which is in fact the only possible mode of attachment on the carbon tetrahedral theory.

At an early stage in this investigation it became necessary to review the evidence for the structure of the unsaturated hydrocarbons resulting from dehydration of the carbinols (III) and (V). Auwers and Treppmann (*Ber.*, 1915, **48**, 1207) dehydrated these carbinols with various agents. In all cases they claimed to have obtained 1-benzyl-Δ^1-*cyclo*hexene (X), which they transformed through its nitrosochloride (XI) (the same nitrosochloride was stated to be obtained from both carbinols) into an unsaturated oxime (XIII), and thence into the corresponding saturated ketone:



(X.) (XI.) (XII.) (XIII.) (XIV.)

* The same 1 : 3 : 3-*bicyclo*nonane system is apparently present in the dicyclic ketones obtained by Rabe (*Ber.*, 1903, **36**, 225; 1904, **37**, 1667, 1671) by condensing ethyl acetoacetate with cyclic ketones and by Stobbe and Rosenburg (*J. pr. Chem.*, 1912, **86**, 226) and by Georgi (*ibid.*, p. 237) by condensing cyclic ketones with $\alpha\beta$-unsaturated ketones. The latter reaction has been revived recently by Rapson and Robinson (J., 1935, 1285), and adapted for the synthesis of polycyclic ketones which probably contain condensed hydroaromatic systems. In none of the cases cited, however, has the structure of the product been proved.

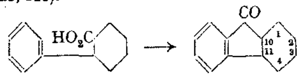


The adjoining structure proposed by Ing (J., 1932, 2778) for cytisine shows very close analogy to the structure of our benz*bicyclo*nonene. The same ring system is apparently present in anagyrine (Ing., J., 1933, 504).

This ketone was not benzoyl*cyclo*hexane and hence was assumed to be 2-benzyl*cyclo*hexanone (XIII). More recently, Prévost, Donzelot, and Balla (*Compt. rend.*, 1934, **198**, 1041) concluded from physical data that the hydrocarbon resulting from the dehydration of phenyl*cyclo*hexylcarbinol (V) with potassium hydrogen sulphate was benzylidene*cyclo*hexane. Moreover, Kurssanoff (*Ber.*, 1931, **64**, 2297) dehydrated this carbinol by pyrolysis of its methyl xanthate and oxidised the product to benzoic acid and *cyclo*hexanone. This also is compatible only with the benzylidene*cyclo*hexane structure.

In the case of the potassium hydrogen sulphate dehydration product of 1-benzyl*cyclo*hexanol we verified completely the results reported by Auwers and Treppmann. The constitution of the final saturated ketone was established by direct comparison with 2-benzyl*cyclo*hexanone prepared from *α-benzylpimelic acid*, which was obtained by hydrolysis of *ethyl 2-benzyl*cyclo*hexanone-2-carboxylate* (XIV). In the case of phenyl*cyclo*hexylcarbinol no satisfactory dehydration product was obtained by the use of potassium hydrogen sulphate, in spite of many attempts. The carbinol was largely converted into high-boiling material (possibly an ether); the small low-boiling fraction was incompletely dehydrated. Similar failure attended the use of anhydrous oxalic acid. The only other method of dehydration reported by Auwers and Treppmann for this carbinol was heating with phosphoric oxide at 160°! By the use of zinc chloride, a reagent employed for this carbinol by Sabatier and Mailhe (*Compt. rend.*, 1904, **139**, 345), we obtained a good yield of hydrocarbon, which contained only 55% of unsaturated compound. Considerable conversion into benz*bicyclo*nonene (VII) had taken place, as was shown by first destroying the unsaturated compound by oxidation with permanganate, and then oxidising the saturated residue with chromic acid, the tricyclic ketone (VIII) being identified by its semicarbazone. The original hydrocarbon mixture obtained by the zinc chloride dehydration gave in rather poor yield a nitrosochloride which was certainly not (XI). Elimination of hydrogen chloride led to a product, the indefinite m. p. of which was depressed by (XII). This definitely establishes the fact that the unsaturated hydrocarbon from phenyl*cyclo*hexylcarbinol and zinc chloride was not benzyl-Δ^1-*cyclo*hexene. It may have been largely the benzylidene*cyclo*hexane obtained by Prévost and his collaborators, and by Kurssanoff, but as we were unable to obtain a constant-melting oxime we did not pursue this question. The essential point is that, contrary to the assertion of Auwers and Treppmann, there is no evidence of the production of benzyl-Δ^1-*cyclo*hexene (X) by migration of the double bond of benzylidene*cyclo*hexane.*

The preparation of hexahydrofluorene by hydrogenation of fluoreneoneoxime with palladium oxide–palladium-black was claimed by Nakamura (*Proc. Imp. Acad. Japan*, 1929, **5**, 469), but by this method we obtained only fluorene and a base. *Hexahydrofluorenone* (XVI) was readily formed by an internal Friedel–Crafts reaction with 2-phenylhexahydrobenzoic acid (XV), an acid first described by Kipping and Perkin (J., 1890, **57**, 316). Our earlier experiments were made with a specimen of this acid obtained by hydrogenating the 2-phenyl-Δ^3-tetrahydrobenzoic acid of Lehmann and Paasche (*Ber.*, 1935, **68**, 1146), but the acid (XV) was more conveniently prepared in quantity by reduction of *o*-phenylbenzoic acid with sodium and amyl alcohol (Ranedo and León, *Anal. Fis. Quim.*, 1925, **23**, 113).

(XV.)  (XVI.)

The isomeric hexahydro-acid obtained by catalytic hydrogenation of *o*-phenylbenzoic acid (Ranedo and León) was not affected by cold concentrated sulphuric acid, and gave no hexahydrofluorenone when its acid chloride was treated with aluminium chloride. Therefore, it was not a stereoisomeride of (XV), but *o*-*cyclo*hexylbenzoic acid (compare the reduction and hydrogenation of *o*-benzylbenzoic acid; Cook, Hewett, and Lawrence, this vol., p. 74). This structure was confirmed by oxidation to phthalic acid.

* Since the present paper was submitted for publication Auwers (*Ber.*, 1935, **68**, 2174) has reaffirmed his previous statement that dehydration of phenyl*cyclo*hexylcarbinol leads to benzyl-Δ^1-*cyclo*hexene.

The ketone (isolated only as the semicarbazone, m. p. 220°) obtained by Vocke (*Annalen*, 1934, **508**, 8) by pyrolysis of hexahydrodiphenic acid is presumably identical with our hexahydrofluorenone (semicarbazone, m. p. 212—213°), as, although *cis*- and *trans*-forms are theoretically possible, stereochemical considerations require an equilibrium in favour of the *cis*-form (compare hexahydro-α-hydrindone; Hückel, Sachs, Yantschulewitsch, and Nerdel, *Annalen*, 1935, **518**, 158, 169).

Hexahydrofluorenone was reduced to *hexahydrofluorene* by Clemmensen's method. The density and refractive index of this hydrocarbon were almost identical with those of the isomeric benz*bicyclo*nonene (VII).

EXPERIMENTAL.

Cyclisation of Benzyl-Δ^1-cyclo*hexenes by Aluminium Chloride.*—1-*Benzyl-2-methyl-*Δ^1-cyclo*hexene* (I; R = H). 2-Methyl*cyclo*hexanone (24·6 g.) was added to an ice-cold Grignard reagent prepared from benzyl chloride (25·2 g.), magnesium turnings (4·8 g.), and anhydrous ether (80 c.c.). After being kept at room temperature for 3 hours, the product was decomposed with ammonium chloride solution. The resulting 1-benzyl-2-methyl*cyclo*hexanol (25 g.; b. p. 115°/0·8 mm.) could not be obtained analytically pure, probably on account of the presence of dibenzyl, which was isolated when the dehydrated carbinol was oxidised with chromic acid. Dehydration by potassium hydrogen sulphate (1·5 parts) at 160—175° (1 hour) led to 1-*benzyl*-2-*methyl*-Δ^1-cyclo*hexene* (95% yield), which formed a colourless liquid, b. p. 158—160°/19 mm., and had $n_D^{17·8°}$ 1·5445 and $d_{4°}^{17·8°}$ 0·9938 * (Found: C, 89·7; H, 9·2. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%). For cyclisation, this unsaturated hydrocarbon (10 g.), dissolved in carbon disulphide (100 c.c.), was treated with anhydrous aluminium chloride (16 g.) and kept at 0° for 3 hours and then over-night at room temperature. The resulting *hydrocarbon* (7 g.) absorbed no bromine, and had b. p. 141°/18 mm., $n_D^{17·8°}$ 1·5438, and $d_{4°}^{17·8°}$ 0·9837 * (Found: C, 90·6; H, 9·7. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

When this saturated hydrocarbon (4 g.) was heated with selenium (5·5 g.) at 300—320° for 100 hours, it became very dark. Distillation gave 1·5 g. of liquid, b. p. 150—160°/20 mm., which appeared to be unchanged hydrocarbon (Found: C, 90·6; H, 9·0%). Palladised charcoal at 300° (7 hours) likewise appeared to have no dehydrogenating action. That cyclisation had occurred in the *o*-position of the benzyl group was shown by oxidation of the hydrocarbon (1 g.) with nitric acid (*d* 1·42; 7 c.c.) and water (15 c.c.) at 180—185° for 5½ hours. The only oxidation product which could be isolated was phthalic acid (Found: C, 57·0; H, 3·7. Calc.: C, 57·9; H, 3·6%). The identification was completed by sublimation as phthalic anhydride (mixed m. p. with an authentic specimen).

1-*Benzyl*-2-*methyl*-5-iso*propyl*-Δ^1-cyclo*hexene* (I; R = Pr^β). Tetrahydrocarvone (for the preparation of which we are indebted to Messrs. Howards and Sons, Ltd.) (38·5 g.) was added to an ice-cold Grignard reagent from benzyl chloride (40 g.), magnesium turnings (7·5 g.), and anhydrous ether (125 c.c.). After being boiled for an hour, the whole was decomposed with ammonium chloride solution. The resulting 1-*benzyl*-2-*methyl*-5-iso*propyl*cyclo*hexanol* (43 g.) formed a colourless viscous liquid, b. p. 140—142°/0·6 mm. (Found: C, 83·1; H, 10·6. $C_{17}H_{26}O$ requires C, 82·85; H, 10·6%). Dehydration to 1-*benzyl*-2-*methyl*-5-iso*propyl*-Δ^1-cyclo*hexene* was not complete with potassium hydrogen sulphate, but was effected by heating with an equal weight of anhydrous zinc chloride at 160°. This hydrocarbon formed a colourless liquid, which absorbed the amount of bromine required for one double bond, and had b. p. 159°/12 mm., $n_D^{15·8°}$ 1·5331, and $d_{4°}^{15·8°}$ 0·9448; whence $[R_L]_D$ = 74·98 (calc., 74·44) (Found: C, 89·6; H, 10·6. $C_{17}H_{24}$ requires C, 89·4; H, 10·6%).

Cyclisation of this compound (I; R = Pr^β) by aluminium chloride at 0° was complete in 5 hours. The resulting saturated hydrocarbon (75% yield) was distilled over sodium and formed a colourless liquid, b. p. 160—161°/13 mm., $n_D^{15·2°}$ 1·5300, and $d_{4°}^{15·2°}$ 0·9607; whence $[R_L]_D$ = 73·35 (calc., 72·71) (Found: C, 89·5; H, 10·4. $C_{17}H_{24}$ requires C, 89·4; H, 10·6%).

This tricyclic hydrocarbon (3·8 g.) was heated with selenium (4 g.) at 310—320° for 40 hours. After distillation over sodium, 2·7 g. of liquid were recovered which had undergone very little dehydrogenation (Found: C, 90·1; H, 9·6%).

*Benz*bicyclo*nonene and its Derivatives.*—For the preparation of this tricyclic hydrocarbon

* No significance attaches to the values for molecular refraction on account of the presence of dibenzyl in the original hydrocarbon. These figures are recorded merely to show the inappreciable change in refractive index after cyclisation.

the standard procedure was as follows: The carbinol (III, IV, or V) was heated with 2 parts of phosphoric oxide at 160° for 20—30 minutes, after which a vacuum was applied and the hydrocarbon distilled. The distillate occasionally contained traces of unsaturated hydrocarbon, which were removed by agitation with concentrated sulphuric acid, followed by redistillation. Formation of the tricyclic hydrocarbon took place during the phosphoric oxide dehydration, and was in no way dependent upon this sulphuric acid treatment. The approximate yields were (a) from 1-benzyl*cyclo*hexanol, 50—70%; (b) from phenyl*cyclo*hexylcarbinol, 30%; from 2-benzyl*cyclo*hexanol, 65%. The last specimen had b. p. 125—126°/10 mm. and $n_D^{14.8°}$ 1·5523.

*Oxidation of benz*bicyclo*nonene to phthalic acid.* A mixture of the hydrocarbon (1 g.), nitric acid (*d* 1·42; 7 c.c.), and water (15 c.c.) was heated at 180° for 5 hours. The tube having been opened, the solution was heated to expel nitrous gases and was then extracted once with ether. The aqueous solution was evaporated to dryness on the water-bath, and the residue recrystallised from water. The crystals (0·1 g.; m. p. 175—180°) were sublimed at 160—190°/14 mm., giving phthalic anhydride, m. p. 127—129° after crystallisation from benzene–*cyclo*hexane.

2 : 3-*Benz*-1 : 3 : 3-bicyclo-Δ^2-*nonen-4-one* (VIII). This could be obtained (1·65 g. of semicarbazone) when the hydrocarbon (4·8 g.) was treated with sodium dichromate (8·5 g.) in boiling acetic acid (50 c.c.) for 2½ hours, and the product fractionated. Better results were obtained by working at room temperature, the same ketone (identified by mixed m. p.'s of the semicarbazone) being formed from the saturated hydrocarbons obtained from 1- and 2-benzyl*cyclo*hexanols and from phenyl*cyclo*hexylcarbinol. The yield was about the same in all cases; on an average, 3·5 g. of semicarbazone were obtained from 10 g. of hydrocarbon. The following experiment is typical: A solution of chromic acid (65 g.) in 80% acetic acid (130 c.c.) was added during an hour to a mechanically stirred solution of benz*bicyclo*nonene (55 g.) in glacial acetic acid (550 c.c.). After being kept at room temperature for a week, the green solution was treated with *iso*propyl alcohol to reduce any excess of chromic acid. Most of the acetic acid was removed under reduced pressure, and the residue was diluted with water and extracted with ether. The extract was washed with dilute sodium carbonate solution and with water, dried, and distilled. The lower fraction, b. p. to 155°/23 mm., was discarded. The ketone fraction (b. p. 100—110°/0·1 mm.; 26·5 g.) was treated with semicarbazide in aqueous-alcoholic solution for 2 hours. The *semicarbazone* (17·7 g.) crystallised from alcohol in small colourless needles, m. p. 222—224° (Found: C, 69·3; H, 7·2; N, 17·1. $C_{14}H_{17}ON_3$ requires C, 69·1; H, 7·0; N, 17·3%). Hydrolysis of this semicarbazone (13 g.) was effected by 3 hours' boiling with a solution of crystalline oxalic acid (32·5 g.) in water (65 c.c.). After distillation in a vacuum, 2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonen-4-one* (VIII) formed a colourless viscous liquid, b. p. 108—110°/0·2 mm., $n_D^{19.9°}$ 1·5770, and $d_{4°}^{19.5°}$ 1·1138; whence $[R_L]_D$ = 55·38 (calc., 54·24). The optical exaltation is in agreement with a structure in which the carbonyl group is directly linked to the aromatic nucleus (Found: C, 83·5; H, 7·6. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The *oxime*, prepared in boiling aqueous-alcoholic solution, crystallised in long colourless needles, m. p. 123—124° (Found: C, 77·8; H, 7·6. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%).

Pure 2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonene* (VII) was prepared by reduction of the pure ketone by Clemmensen's method (8 g. of ketone, 24 g. of amalgamated zinc, and 40 c.c. of concentrated hydrochloric acid were boiled for 6 hours). The pure hydrocarbon (3 g.) was a colourless mobile liquid, b. p. 85°/0·3 mm., 123°/15 mm., $n_D^{14°}$ 1·5580, $d_{4°}^{14°}$ 1·020; whence $[R_L]_D$ = 54·47 (calc., 54·23) (Found: C, 90·3; H, 9·5. $C_{13}H_{16}$ requires C, 90·6; H, 9·4%).

Attempted dehydrogenation of 2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonene*. The failure to effect dehydrogenation with selenium was recorded in our earlier communication (*loc. cit.*). When the hydrocarbon (sample prepared from 2-benzyl*cyclo*hexanol; 2 g.) was heated with platinum-black (1 g.) for 10 hours in an atmosphere of carbon dioxide, 1·5 g. of hydrocarbon were recovered which seemed to be entirely unchanged. Furthermore, when this hydrocarbon was passed over platinised asbestos (Zelinsky and Borisoff, *Ber.*, 1924, 57, 150) at 340—360° in an apparatus similar to that described by Ehrenstein (*loc. cit.*), no hydrogen was liberated and the hydrocarbon appeared to be unchanged. The activity of the catalyst was demonstrated by the fact that when decalin was afterwards used, hydrogen was freely liberated and naphthalene was formed.

3′-*Nitro*-2 : 3-*benz*-1 : 3 : 3-bicyclo-Δ^2-*nonen-4-one* (IX; X = NO_2). This was obtained when the ketone was boiled with concentrated nitric acid (10 parts) for 10 minutes, or by nitration with nitric acid in sulphuric acid. The best results were obtained when the ketone (10 g.)

was added dropwise to nitric acid (*d* 1·5; 100 c.c.). Heat was evolved, but no external cooling was applied. After ¾ hour the solution was heated on the water-bath for ½ hour, and then cooled and poured into water. The *nitro*-compound crystallised from alcohol in colourless plates, m. p. 118·5—119·5° (Found: C, 67·65; H, 5·6. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7%).

3'-Amino-2 : 3-benz-1 : 3 : 3-bicyclo-Δ²-nonen-4-one (IX; X = NH_2). A solution of the nitro-compound (5 g.) in alcohol (25 c.c.) was slowly added to a solution of stannous chloride (30 g.) in concentrated hydrochloric acid (25 c.c.), heated on the water-bath. Heating was continued for ½ hour, and the solution was diluted with water, made strongly alkaline, and extracted with ether. The extract was dried (sodium sulphate), the ether removed, and the residue recrystallised from *cyclo*hexane with a little benzene. The *amine* (3·5 g.) formed lemon-yellow leaflets, m. p. 122·5—123·5°, readily soluble in cold dilute mineral acids to give colourless solutions (Found: C, 77·6; H, 7·7. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%).

A boiling solution of this amine (0·5 g.) in glacial acetic acid (5 c.c.) was oxidised by dropwise addition of a solution of chromic acid (3 g.) in 80% acetic acid (6 c.c.). The whole was boiled for 1½ hours, the acetic acid removed under reduced pressure, the residue dissolved in water, the solution filtered, and the filtrate extracted four times with ether. After removal of the ether, the residue was heated at 100° under reduced pressure to remove the last traces of acetic acid. The non-volatile residue was dissolved in water, boiled with charcoal, and the filtered solution was evaporated to dryness. The resulting *cis*-hexahydro*iso*phthalic acid crystallised from water in small colourless leaflets, m. p. 160—162°, not depressed by the acid obtained from the hydroxy-ketone (below).

3'-Hydroxy-2 : 3-benz-1 : 3 : 3-bicyclo-Δ²-nonen-4-one (IX; X = OH). An ice-cold solution of the amino-ketone (2 g.) in *N*-sulphuric acid (25 c.c.) was diazotised with aqueous sodium nitrite (0·7 g. in 3 c.c.). The diazonium sulphate separated partly as an orange crystalline precipitate, a solution of which gave a dark red precipitate with alkaline β-naphthol. After ½ hour, urea (0·1 g.) was added, and the suspension was slowly added to boiling *N*-sulphuric acid (400 c.c.). After boiling for a few minutes, the whole was cooled and extracted with ether. The phenol was removed from the ethereal extract by shaking with dilute sodium hydroxide solution, and the alkaline solution was boiled with charcoal, filtered, and acidified. After cooling, the crystalline *hydroxy-ketone* (1·45 g.) was collected, washed, and recrystallised from aqueous alcohol. For analysis, a little of the resulting leaflets was recrystallised from benzene–*cyclo*hexane, forming a colourless crystalline powder, m. p. 160·5—161·5° (Found: C, 77·4; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%).

For oxidation, a solution of this phenol (IX; X = OH) (0·82 g.) in water (25 c.c.), containing potassium hydroxide (0·4 g.), was stirred mechanically during addition of an aqueous solution of potassium permanganate (5·55 g. in 110 c.c.). The oxidation was completed by heating on the water-bath for 20 minutes. The filtered solution was acidified with hydrochloric acid and evaporated to dryness on the water-bath. The residue was extracted with water, filtered from a trace of resinous matter, and extracted five times with ether. The extract was dried (sodium sulphate), the ether removed, and the residue recrystallised from a little water, with charcoal. The resulting *cis*-hexahydro*iso*phthalic acid (0·25 g.) was recrystallised from benzene, forming a colourless powder, m. p. 161·5—162·5°, not depressed by an authentic sample (Found: C, 56·5; H, 7·0. Calc.: C, 55·8; H, 7·0%). The identification was completed by conversion into the anhydride, m. p. 185—186° (Perkin, J., 1891, **59**, 813, gives 187—189°), which by brief warming with aniline gave the anilic acid, m. p. 210—211°, described by Komppa (*Ann. Acad. Sci. Fennicae*, 1933, **37**, *A*, No. 6, 1).

The authentic specimen of *cis*-hexahydro*iso*phthalic acid was prepared by hydrogenation of *iso*phthalic acid (5 g.) in alcoholic solution (250 c.c.) with a platinum oxide catalyst (1 g.) at 4 atmospheres' pressure. Hydrogenation was complete in 2 hours, and the *cis*-hexahydro-acid was purified through its sparingly soluble calcium salt (Perkin, *loc. cit.*).

Unsaturated Hydrocarbons from 1-Benzylcyclohexanol and Phenylcyclohexylcarbinol.—*2-Benzylcyclohexanone from 1-benzyl-Δ¹-cyclohexene.* The nitrosochloride of benzyl*cyclo*hexene (obtained from 1-benzyl*cyclo*hexanol by dehydration with potassium hydrogen sulphate) was prepared by addition during 1 hour of a mixture of acetic acid (35 c.c.) and fuming hydrochloric acid (35 c.c.) to a mixture of hydrocarbon (30 g.), glacial acetic acid (30 c.c.), and amyl nitrite (24 c.c.), cooled in ice and salt. After an hour a little methyl alcohol was added and the nitrosochloride (12·5 g.) was collected and drained on porous porcelain; it then had m. p. 97—102°. This nitrosochloride (XI) was sufficiently stable to be recrystallised in small amounts from benzene, from which it separated in snow-white needles, m. p. 116—117° (Auwers and

Treppmann, *loc. cit.*, give 110°) (Found: C, 64·85; H, 6·5. Calc. for $C_{13}H_{16}ONCl$: C, 65·7; H, 6·8%). For elimination of hydrogen chloride, a solution of the nitrosochloride (12 g.) in pyridine (60 c.c.) was boiled for 3 hours. After cooling, and dilution with water, the oxime (XII) crystallised (4·6 g.); recrystallised from methyl alcohol, it formed stout colourless needles, m. p. 138·5—139·5°. This was clearly the oxime obtained by Auwers and Treppmann, who give m. p. 136—138°. Hydrolysis to the unsaturated ketone was effected by boiling 6*N*-sulphuric acid in 1½ hours, and the distilled ketone (bath at 180°; 0·4 mm.) was hydrogenated in ethereal solution with a palladium-black catalyst. The resulting saturated ketone (XIII) gave, in good yield, a semicarbazone, m. p. 165—166°, not depressed by the semicarbazone of 2-benzyl*cyclo*hexanone prepared as described below.

*Dehydration of phenyl*cyclo*hexylcarbinol with zinc chloride.* A mixture of the carbinol (20 g.) and powdered anhydrous zinc chloride (40 g.) was heated for an hour at 170—180°. While still warm, the liquid was poured off and distilled in a vacuum, and then redistilled over sodium (Found: C, 90·3; H, 9·3. Calc. for $C_{13}H_{16}$: C, 90·6; H, 9·4%). The hydrocarbon mixture (15 g.) had b. p. 90—91°/5 mm., $n_D^{12·8°}$ 1·5460, and $d_{4°}^{12·8°}$ 0·9656. These values are in good agreement with those given by Auwers and Treppmann, but this is of no significance, as the product was not homogeneous.

This hydrocarbon mixture (11 g.) was treated with amyl nitrite and hydrochloric acid as described for benzyl-Δ^1-*cyclo*hexene. The resulting nitrosochloride (1 g.) separated slowly from its solution in benzene as a white powder, m. p. 115—117° (decomp.); the mixed m. p. with the nitrosochloride of benzyl*cyclo*hexene was 106—108° (decomp.). Elimination of hydrogen chloride with boiling pyridine led to a product which crystallised in colourless needles, m. p. 128—132° after sintering; the mixed m. p. with benzyl*cyclo*hexenoneoxime (XII) was 110—115°. This experiment was repeated several times, with consistent results. The oxime mixture could be partly separated into higher-melting fractions. For example, by extraction with boiling *cyclo*hexane an insoluble residue, m. p. 155—160°, was obtained, and the filtrate deposited colourless needles, m. p. 147—155°. No homogeneous sharp-melting substance could be isolated from the small amount of material available.

The presence of benz*bicyclo*nonene (VII) in the hydrocarbon mixture (iodine value, 79. Calc. for one double bond, 148) obtained by dehydrating phenyl*cyclo*hexylcarbinol was shown as follows: The hydrocarbon mixture (8 g.) was heated on the water-bath with 5% aqueous potassium permanganate, more being added as long as it was decolorised rapidly. The manganese dioxide was reduced by sulphur dioxide, and the oil was extracted with ether, the extract dried, and the ether removed. The resulting liquid (3·5 g.) was almost completely saturated, aud after oxidation with cold chromic acid in the usual way it gave 0·75 g. of the semicarbazone of benz*bicyclo*nonenone (VIII).

*2-Benzyl*cyclo*hexanone and 2-Benzyl*cyclo*hexanol.—Ethyl 2-benzyl*cyclo*hexanone-2-carboxylate.* The sodio-compound prepared from ethyl *cyclo*hexanone-2-carboxylate (34 g.) and powdered sodium (4·6 g.) in benzene (100 c.c.) was boiled for 5 hours with benzyl chloride (25·2 g.). After decomposition with water, the washed benzene solution was dried and distilled. *Ethyl 2-benzyl*cyclo*hexanone-2-carboxylate* (XIV), obtained in 80% yield, formed a colourless liquid, b. p. 144—145°/0·4 mm., which slowly crystallised. After recrystallisation from light petroleum and then from methyl alcohol it had m. p. 34·5—35° (Found: C, 73·8; H, 7·5. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·75%). The *semicarbazone* had m. p. 182—183° (Found: C, 64·3; H, 8·35. $C_{17}H_{23}O_3N_3$ requires C, 64·3; H, 7·3%). *α-Benzylpimelic acid*, obtained by hydrolysis of the keto-ester with alcoholic potash, separated from water in small colourless crystals, m. p. 81—82° (Found: C, 66·8; H, 7·2. $C_{14}H_{18}O_4$ requires C, 67·0; H, 7·25%).

2-Benzyl*cyclo*hexanone (XIII) was formed when α-benzylpimelic acid (75 g.) was distilled from a metal-bath at 360—380°. The ketone was purified through its sodium bisulphite compound, and was then distilled, yielding 26 g. of a colourless liquid, b. p. 155°/10 mm. (Found: C, 82·7; H, 8·7. Calc.: C, 82·9; H, 8·6%). The semicarbazone had m. p. 167—168°, in agreement with other workers who prepared this ketone by other methods (Tiffeneau and Porcher, *Bull. Soc. chim.*, 1922, **31**, 330; Cornubert and Maurel, *ibid.*, 1931, **49**, 1512, give 170—171°; Poggi and Saltini, *Gazzetta*, 1932, **62**, 684).

*2-Benzyl*cyclo*hexanol.* Water was added during 4 hours to a mechanically stirred mixture of 2-benzyl*cyclo*hexanone (26 g.), pure ether (100 c.c.), and thin slices of sodium (26 g.). The ethereal solution was washed, dried, and distilled. *2-Benzyl*cyclo*hexanol* (IV), b. p. 154°/11 mm., crystallised from light petroleum in long colourless needles (20 g.), m. p. 75·5—76° (Found: C, 81·9; H, 9·5. $C_{13}H_{18}O$ requires C, 82·1; H, 9·8%). A more convenient route to this carbinol was subsequently found (Cook, Hewett, and Lawrence, this vol., p. 75).

Dehydrogenation of 2-Benzyloctalin * *and 2-Benzyldecalin.*—*trans-2-Benzyl-2-decalol.* *trans*-β-Decalone (15 g.) was added to an ice-cold Grignard solution prepared from benzyl chloride (12·5 g.), magnesium turnings (2·5 g.) and anhydrous ether (65 c.c.). The product was boiled for 2 hours, and decomposed with ammonium chloride solution. The dried ethereal solution was distilled, the carbinol fraction (16 g.) having b. p. 171°/6 mm. For characterisation, the 3 : 5-*dinitrobenzoate* was prepared by brief heating at 100° with 3 : 5-dinitrobenzoyl chloride in pyridine. It crystallised from alcohol in colourless needles, m. p. 162·5—164° (Found: C, 66·1; H, 6·0. $C_{24}H_{26}O_6N_2$ requires C, 65·7; H, 6·0%).

2-*Benzyloctalin* was obtained by dehydration of the aforesaid carbinol with potassium hydrogen sulphate at 160—170° (2 hours). It was distilled over zinc chloride and then over sodium, forming a colourless liquid, b. p. 151°/6 mm., $n_D^{12·6°}$ 1·5520 (Found: C, 90·0; H, 9·8. $C_{17}H_{22}$ requires C, 90·2; H, 9·8%). For dehydrogenation, the hydrocarbon (2·2 g.) was heated with selenium (5·7 g.) at 310—320° for 48 hours. The product was distilled over sodium in a vacuum, and the distillate treated with alcoholic picric acid. The picrate of 2-benzylnaphthalene had m. p. 93°, in agreement with Roux (*Ann. Chim.*, 1887, **12**, 331), and the regenerated hydrocarbon, after crystallisation from alcohol, had m. p. 55·5°, in agreement with Vincent and Roux (*Bull. Soc. chim.*, 1883, **40**, 165) and with Dziewoński and Wodelski (*Rocz. Chem.*, 1932, **12**, 369).

2-*Benzyldecalin.* A solution of 2-benzyloctalin (11 g.) in glacial acetic acid (50 c.c.) was shaken with hydrogen and palladium-black (from 1 g. of palladous chloride) for 6 hours. The product was freed from solvent, and its benzene solution was washed with 80% sulphuric acid until no further colour was developed by fresh portions of acid. After distillation over sodium, 2-*benzyldecalin* formed a colourless liquid, b. p. 173—175°/10 mm. (Found: C, 89·6; H, 10·35. $C_{17}H_{24}$ requires C, 89·4; H, 10·6%). This hydrocarbon was unchanged by heating with an equal weight of selenium at 320—330° for 20 hours (Found: C, 89·2; H, 10·0%), but was dehydrogenated to 2-benzylnaphthalene (identified by m. p. of hydrocarbon and picrate) by heating at 300—305° for 6 hours with one-third of its weight of platinum-black.

Synthesis of Hexahydrofluorene.—*2-Phenylhexahydrobenzoic acid from α-phenylbutadiene.* 2-Phenyl-Δ^3-tetrahydrobenzaldehyde was prepared from α-phenylbutadiene and acraldehyde (Lehmann and Paasche, *Ber.*, 1935, **68**, 1146) and was oxidised in the cold by chromic acid in acetic acid (not by warming on the water-bath as specified by Lehmann and Paasche). The acidic product was distilled. Fractional crystallisation of the distillate furnished a small amount of an acid, m. p. 119·5—120·5°. This was probably the acid (m. p. 122°) obtained by Lehmann and Paasche from phenylbutadiene and acrylic acid. They stated that this acid was 3-phenyl-Δ^4-tetrahydrobenzoic acid, as it was different from the 2-phenyl-Δ^3-tetrahydrobenzoic acid formed by oxidation of the aldehyde, but it seems equally probable that the two acids are stereoisomeric.

Hydrogenation of the crude distilled acids from the above oxidation, by palladium-black in acetic acid, gave 2-phenylhexahydrobenzoic acid, m. p. 105—107° (from light petroleum). This acid did not depress the m. p. of the acid obtained by reduction of *o*-phenylbenzoic acid with sodium and amyl alcohol (Ranedo and León, *loc. cit.*) and the latter route proved to be more convenient for preparative purposes. As it seemed possible that the acid, m. p. 102—103°, obtained by Ranedo and León by catalytic hydrogenation of *o*-phenylbenzoic acid was stereoisomeric with the above hexahydro-acid, their experiment was repeated. The new hexahydro-acid was purified by dissolution in concentrated sulphuric acid, which sulphonated or dehydrated impurities but did not affect the acid in question. The acid so purified had m. p. 104°, and its structure as *o-cyclo*hexylbenzoic acid was established by the fact that it was slowly oxidised to phthalic acid (isolated as the anhydride) by boiling 5% alkaline potassium permanganate solution.

Hexahydrofluorenone (XVI). The conversion of 2-phenylhexahydrobenzoic acid into this ketone (identified by mixed m. p. of the semicarbazone) was carried out with specimens of the acid prepared from phenylbutadiene, and also from *o*-phenylbenzoic acid. The acid (XV) (20 g.) was converted into its chloride by 1 hour's boiling with thionyl chloride (100 c.c.), excess of thionyl chloride being then removed on the water-bath under reduced pressure. An ice-cold carbon disulphide solution (100 c.c.) of the crystalline chloride was treated with anhydrous aluminium chloride (13·5 g.), kept at 0° for 3 hours, and then decomposed with ice and hydrochloric acid. After being washed (sodium carbonate solution removed a little unchanged acid) and dried, the carbon disulphide was removed, and the residue distilled. The distillate,

* The preparation and dehydrogenation of 2-benzyloctalin were carried out by Dr. A. Dansi.

b. p. 130—132°/1 mm. (14 g.), crystallised. 1 : 2 : 3 : 4 : 10 : 11-*Hexahydrofluorenone* (XVI) crystallised from light petroleum in long colourless needles, m. p. 41·5—42° (Found : C, 83·4; H, 7·6. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The *semicarbazone* formed a yellowish crystalline powder (from alcohol), m. p. 212—213° (Found : C, 69·5; H, 7·1; N, 18·0. $C_{14}H_{17}ON_3$ requires C, 69·1; H, 7·0; N, 17·3%). An *oxime* prepared from the crude distilled ketone formed colourless needles (from *cyclo*hexane), m. p. 183—185° (Found : C, 78·0; H, 7·3. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%). Subsequent attempts to prepare this oxime from the pure re-crystallised ketone gave products of indefinite m. p., *ca.* 130—135°.

1 : 2 : 3 : 4 : 10 : 11-*Hexahydrofluorene*. The foregoing ketone (10 g.) was reduced by boiling for 5 hours with concentrated hydrochloric acid (20 c.c.), water (40 c.c.), and amalgamated zinc (30 g.), concentrated hydrochloric acid (5 c.c.) being added after each hour. The hydrocarbon was distilled in steam, separated from the distillate with ether, dried, and distilled. *Hexahydrofluorene* (8·2 g.) formed a colourless mobile liquid, b. p. 127°/15 mm., $n_D^{10·9°}$ 1·5572, $d_{4°}^{10·9°}$ 1·019; whence $[R_L]_D$ = 54·37 (calc., 54·23) (Found : C, 90·2; H, 9·2. $C_{13}H_{16}$ requires C, 90·6; H, 9·4%).

Dehydrogenation of hexahydrofluorene. (a) A mixture of hexahydrofluorene (0·7 g.) and Adams's platinum oxide (0·1 g.), reduced with hydrogen, was heated at 250—260° for 1½ hours. Evolution of hydrogen was very brisk at this temperature. Even at 160° some gas was liberated. After recrystallisation from alcohol, the product had m. p. 113·5—114·5°, alone or mixed with an authentic specimen of fluorene, and gave a picrate, m. p. 80—81° (*lit.*, 80—82°).

(b) Dehydrogenation of hexahydrofluorene with an equal weight of selenium at 300—320° for 15 hours gave fluorene in good yield.

Oxidation of hexahydrofluorene with chromic acid in acetic acid under the conditions used for benz*bicyclo*nonene led to high-boiling resinous products which could not be distilled without decomposition. No hexahydrofluorenone could be isolated.

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16. *A New Synthetic Route to Hydroaromatic Ketones related to Anthracene and Phenanthrene.*

By J. W. COOK, C. L. HEWETT, and C. A. LAWRENCE.

THE objects of this investigation were (a) the preparation of stereochemically homogeneous polycyclic hydroaromatic compounds which might serve as a starting point in a study of the stereochemistry of completely hydrogenated polycyclic systems, and (b) the exploitation of new methods of synthesis of compounds derived from the carcinogenic hydrocarbon 3 : 4-benzphenanthrene. The latter project was checked by the unforeseen chemical behaviour of 2-(1'-naphthyl)*cyclo*hexanol, and we report now only the preparation of this carbinol, the properties of which are being further examined.

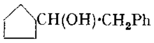
As a starting point in our study of the stereochemistry of perhydrophenanthrene derivatives we required the hexahydrophenanthrone (V), which should exist in two racemic forms (*cis* and *trans* with reference to the points of fusion of the two reduced rings). A method has been devised whereby one of these forms may be obtained readily in moderate amount. The other form has been isolated as a by-product, and it may be possible to modify the stages so that this will become the main product.

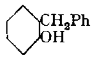
Obvious intermediate compounds to use in the synthesis of hexahydrophenanthrone were 2-phenyl*cyclo*hexanol and 2-phenyl*cyclo*hexanone, but published methods of preparation of these substances (see, for example, von Braun, Gruber, and Kirschbaum, *Ber.*, 1922, **55**, 3670; Brazidec, *Bull. Soc. chim.*, 1915, **17**, 104; Lévy and Sfiras, *Compt. rend.*, 1928, **187**, 45) were inconvenient for our purpose. By the action of phenylmagnesium bromide on *cyclo*hexene oxide Bedos (*Bull. Soc. chim.*, 1926, **39**, 292) obtained a very poor yield of impure 2-phenyl*cyclo*hexanol. The reason for this bad result is evident from subsequent investigations on the action of Grignard reagents on *cyclo*hexene oxides and 2-chloro*cyclo*hexanols, the normal consequence of these reactions being contraction of the

ring with the formation of *cyclo*pentylcarbinols (Vavon and Mitchovitch, *Compt. rend.*, 1928, **186**, 702; Bedos, *ibid.*, 1929, **189**, 255; contrast Godchot and Bedos, *ibid.*, 1924, **178**, 1184). The presence of magnesium halide is a factor in promoting these rearrangements, for *cyclo*hexene oxide can be transformed into *cyclo*pentylformaldehyde by ethereal magnesium bromide (Bedos, *loc. cit.*; compare Arbusow, *Ber.*, 1935, **68**, 1434). Moreover, Bartlett and Berry (*J. Amer. Chem. Soc.*, 1934, **56**, 2683) have shown that ring contraction can be avoided, and the normal substituted *cyclo*hexanols obtained, by the use of halide-free magnesium alkyls. From these and other cognate investigations (Henry, *Compt. rend.*, 1907, **145**, 21; Godchot and Cauquil, *ibid.*, 1928, **186**, 375, 955; Tiffeneau and Tchoubar, *ibid.*, 1934, **198**, 941; Vavon and collaborators, *Bull. Soc. chim.*, 1929, **45**, 965; 1930, **47**, 904; 1932, **51**, 994) it seems that rearrangement occurs when the second stage of the interaction between the Grignard reagent and the oxide or chlorohydrin is brought about by heating the intermediate compound, after distillation of the ether (compare Grignard, *Compt. rend.*, 1903, **136**, 1260; 1905, **141**, 44; *Ann. Chim.*, 1907, **10**, 23).

We have re-examined the reaction between phenylmagnesium bromide and *cyclo*hexene oxide. The usual phenomena were observed. A precipitate of the intermediate compound was rapidly formed, which gave apparently 2-bromo*cyclo*hexanol when decomposed with water, whereas a violent reaction set in when this intermediate compound was heated on the water-bath. The violence could be moderated by the use of anisole as a solvent, but the carbinol fraction subsequently isolated gave no crystalline dinitrobenzoate, and no crystalline semicarbazone could be obtained from the chromic acid oxidation product. Evidently rearrangement to phenyl*cyclo*pentylcarbinol (Edwards and Reid, *J. Amer. Chem. Soc.*, 1930, **52**, 3236) had taken place to a considerable extent. This rearrangement was completely avoided, and 2-phenyl*cyclo*hexanol was obtained in almost quantitative yield, when phenyl-lithium was substituted for phenylmagnesium bromide. 2-(1′-*Naphthyl*)-cyclo*hexanol* was likewise obtained from 1-naphthyl-lithium and *cyclo*hexene oxide. These results corroborate the conclusions of Bartlett and Berry (*loc. cit.*) that the presence of halide is necessary for the molecular rearrangements which occur under the influence of Grignard reagents.

We have also examined the action of benzylmagnesium chloride on 2-chloro*cyclo*hexanol and *cyclo*hexene oxide, with rather remarkable results. In the former case the usual two-stage reaction occurred, attended by complete rearrangement. The resulting *carbinol* was oxidised to a *ketone* which differed from the known 2-benzyl*cyclo*hexanone, and hence by analogy the carbinol is represented by formula (I). The Grignard reagent

(I.) 

 (II.)

from benzyl chloride reacted readily with *cyclo*hexene oxide with liberation of heat, the phenomena being parallel to those observed in the reactions with aryl-lithiums. Hence it seemed likely that complete reaction, and not merely the first stage, had taken place. This proved to be the case, for decomposition with water gave a 50% yield of 2-benzyl-*cyclo*hexanol (II), identical with that prepared by a method which establishes its structure (Cook and Hewett, this vol., p. 69). The only analogous case in the recent literature, of condensation between a Grignard reagent and *cyclo*hexene oxide without rearrangement, is given by Fulton and Robinson (J., 1933, 1463), who believed that they had obtained 2-β-phenylethyl*cyclo*hexanol with β-phenylethylmagnesium bromide. However, the experimental description given by these authors is typical of a reaction which *is* accompanied by rearrangement. Professor Robinson has kindly undertaken a re-investigation of this example, with results which are reported on p. 80.

The abnormal behaviour of benzylmagnesium chloride cannot be ascribed to the equilibrium

$$2RMgX \rightleftharpoons MgX_2 + MgR_2$$

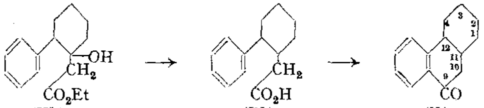
being predominantly in favour of dibenzylmagnesium as, although this is the case, the following figures, quoted from Johnson and Adkins (*J. Amer. Chem. Soc.*, 1932, **54**, 1944;

compare Schlenk, *Ber.*, 1931, **64**, 734), show that the position of equilibrium is much the same with all three compounds under discussion :

Halide.	Yield of Grignard reagent (%).	% present as R_2Mg.
Benzyl chloride	93·6 ± 0·7	73·4 ± 2·5
Bromobenzene	94·7 ± 0·5	75·8 ± 2·7
β-Phenylethyl bromide	91·6 ± 0·1	76·0 ± 2·2

The logical conclusion to be drawn from our results is that with Grignard solutions from benzyl chloride the dialkylmagnesium is more reactive than the alkylmagnesium halide towards *cyclo*hexene oxide, whereas in the other two examples the reverse is the case, disturbance of the equilibrium by combination with the more active component of the Grignard solution being rapidly followed by conversion of the less active into the more active component. That some, at any rate, of the Grignard reagent from benzyl chloride reacted in the form of benzylmagnesium chloride was shown by the isolation of a fraction corresponding with 2-chloro*cyclo*hexanol in 20% yield. From the work of Bartlett and Rosenwald (*J. Amer. Chem. Soc.*, 1934, **56**, 1990) this should be the *cis*-compound, and this was probably largely true, as, although a small amount of the phenylurethane of ordinary (*trans*) 2-chloro*cyclo*hexanol was isolated, there was obtained a much larger quantity of a lower-melting phenylurethane, not isolated in the pure state.

For the synthesis of *hexahydrophenanthrone*, 2-phenyl*cyclo*hexanol was oxidised to 2-phenyl*cyclo*hexanone, which was then condensed with ethyl bromoacetate by the Reformatsky reaction, to give *ethyl 2-phenyl*cyclo*hexanol-1-acetate* (III). This was dehydrated to the corresponding unsaturated *ester*, which, after hydrolysis, was hydrogenated to *2-phenyl*cyclo*hexylacetic acid* (IV), the latter being rapidly dehydrated by concentrated sulphuric acid to 9-*keto*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (hexahydrophenanthrone, V). This ketone could not be obtained crystalline, but gave crystalline derivatives.



(III.) (IV.) (V.)

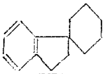
When 2-phenyl*cyclo*hexanol was treated with phosphorus tribromide, and the product (obtained in poor yield) condensed with ethyl potassiomalonate, followed by hydrolysis and decarboxylation, there was obtained a small amount of an *acid*, probably stereoisomeric with (IV). The same acid was doubtless present in the lower-melting fractions from the mother-liquors of the crystallisation of (IV), but could not be isolated in the pure state. However, cyclisation of this mixture gave a product, from which a crystalline *isomeride* of (V) was isolated. We are engaged in a determination of the configurations of the two tricyclic ketones (V).

The non-crystalline hexahydrophenanthrone (V) was hydrogenated to a crystalline *octahydro-9-phenanthrol*, which was dehydrogenated by platinum-black at 300° to 9-phenanthrol, and was dehydrated to *hexahydrophenanthrene*, which in its turn was dehydrogenated to phenanthrene.

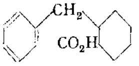
Although there can be little doubt that the hydrocarbon resulting from cyclisation of β-phenylethyl-Δ^1-*cyclo*hexene is mainly *as.*-octahydrophenanthrene (Cook and Hewett, J., 1933, 1108), the evidence of its structure depends upon dehydrogenation of the hydrocarbon or of its derivatives (Cook and Haslewood, J., 1935, 767) to completely aromatic compounds of established structure. Independent confirmation has now been afforded by oxidation of this hydrocarbon to the ketone (V), identical with the non-crystalline ketone prepared from 2-phenyl*cyclo*hexanone. By fractional crystallisation of the oximes there were obtained not only the *oxime*, m. p. 124°, of (V), but also an *oxime*, m. p. 187°, which was not the oxime of the stereoisomeric ketone (V). This new oxime is possibly that of a ketone derived from the spirocyclic hydrocarbon (VI), the presence of which would be

expected in the hydrocarbon mixture used for oxidation, although the analytical data for the oxime, m.p. 187°, are in much better agreement with a compound containing two hydrogen atoms less.

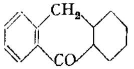
Conversion of 2-benzyl*cyclo*hexanol into the corresponding 1-chloro-2-benzyl*cyclo*hexane was attended by partial dehydration, so that the chloro-compound was contaminated with hydrocarbon. When carbon dioxide was passed into a Grignard solution prepared from this crude chloro-compound, a mixture of the two stereoisomeric *2-benzylhexahydrobenzoic acids* (VII) resulted. The partial Walden inversion had probably occurred in the preparation of the chloro-compound. The higher-melting acid (134°), obtained more readily by reduction of *o*-benzylbenzoic acid by sodium and amyl alcohol, was rapidly dehydrated by concentrated sulphuric acid to a mixture of *hexahydroanthrones* (VIII). The more abundant constituent, m. p. 109°, was also obtained by an internal Friedel–Crafts reaction with the acid, m. p. 134°.



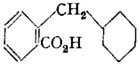
(VI.)



(VII.)



(VIII.)



(IX.)

The lower-melting 2-benzylhexahydrobenzoic acid (86—88°), not obtained completely pure, was also dehydrated to a mixture of the hexahydroanthrone, m. p. 109°, and a larger proportion of the more soluble isomeride, m. p. 80°. The formation of both hexahydroanthrones in these reactions evidently involves interconversion of the ketones through an intermediate enolic form, as in the transformation of *cis*-α-decalone into *trans*-α-decalone (Hückel, *Annalen*, 1925, **441**, 31), and of 3 : 6-diketocholanic acid into the *allo*-compound (Windaus and Bohne, *Annalen*, 1923, **433**, 278; Windaus, *ibid.*, 1926, **447**, 244). The two stereoisomeric hexahydroanthrones were characterised by their sharp-melting *oximes*, and anthracene and anthraquinone were obtained from both of them by dehydrogenation, and then oxidation. The isolation of two oximes is of interest, as Hückel (*loc. cit.*) has shown that *cis*- and *trans*-α-decalones both give the same oxime. We are seeking experimental proof that the hexahydroanthrone, m. p. 109°, is the *trans*-compound.

On account of the large amount of hydrocarbon formed in the conversion of 2-benzyl*cyclo*hexanol into its chloride, the *bromide* was substituted in a succeeding experiment. This was obtained in 44% yield by means of phosphorus tribromide, and in the hope of improving the yield in the next stage, ethyl chloroformate was substituted for carbon dioxide in the Grignard condensation. No better yield was obtained. The esters formed in the reaction were hydrolysed, and the mixture of acids was separated by fractional crystallisation into *trans*-2-benzylhexahydrohenzoic acid, m. p. 134°, and a third *isomeride*, m. p. 140°. None of the *cis*-acid was apparently formed. Stereochemical theory cannot easily accommodate a third acid of structure (VII). The new acid, m. p. 140°, which was completely sulphonated by brief treatment with concentrated sulphuric acid, may be 4-benzylhexahydrobenzoic acid, formed by migration of bromine in the intermediate bromo-compound (compare Nenitzescu and Gavăt, *Annalen*, 1935, **519**, 260). Experiments to test this hypothesis are in progress.

o-Benzylbenzoic acid was readily hydrogenated at ordinary pressure by Adams's platinum oxide catalyst to a hexahydro-acid, m. p. 96°, different from all three hexahydro-acids already mentioned. This was saturated, and was unattacked by cold concentrated sulphuric acid, and was therefore *ω-cyclohexyl-o-toluic acid* (IX). Confirmation of this was afforded by oxidation by alkaline permanganate to phthalic acid. It is remarkable that chemical reduction should attack the carboxylated ring of *o*-benzylbenzoic acid, whereas catalytic hydrogenation attacks the other ring. An analogous case is *o*-phenylbenzoic acid, which behaves in the same way (Cook and Hewett, this vol., p. 65).

EXPERIMENTAL.

*Carbinols from 2-Chloro*cyclo*hexanol and* cyclo*Hexene Oxide*.—The materials used in these experiments were prepared by Mr. F. Goulden by the procedure given in "Organic Syntheses" (Collective Vol. I, pp. 151, 179).

*Benzyl*cyclo*pentylcarbinol* (I). 2-Chloro*cyclo*hexanol (10 g.) was added to an ice-cold Grignard reagent prepared from benzyl chloride (19 g.), magnesium turnings (3·6 g.), and anhydrous ether (100 c.c.). After being kept over-night at room temperature, the ether was distilled off and the residue was heated on the water-bath for an hour. The product was decomposed by shaking with ether and ammonium chloride solution, and the ethereal extract was washed, dried, and distilled. The carbinol (7·7 g.) formed a viscous liquid, b. p. 166—169°/20 mm., which crystallised when strongly cooled. The 3 : 5-*dinitrobenzoate*, prepared by heating a mixture of this carbinol (4 g.) with 3 : 5-dinitrobenzoyl chloride (6 g.) in pure pyridine (20 c.c.) at 100° for ½ hour, crystallised from alcohol in thin colourless needles, m. p. 100·5—101·5° (Found : C, 62·3; H, 5·4. $C_{20}H_{20}O_6N_2$ requires C, 62·5; H, 5·25%). Hydrolysis of this ester with boiling aqueous-alcoholic potash gave pure *benzyl*cyclo*pentylcarbinol* (I), which was distilled at 0·1 mm. from a bath at 120°. The colourless distillate crystallised on standing, and had m. p. 30° (Found : C, 81·7; H, 9·65. $C_{13}H_{18}O$ requires C, 82·0; H, 9·5%). For oxidation to the ketone, a solution of chromic acid (0·4 g.) in 80% acetic acid (1·5 c.c.) was added dropwise to a solution of the carbinol (0·7 g.) in glacial acetic acid (10 c.c.), and the whole was kept at room temperature over-night. The oxidation product was isolated and treated with semicarbazide hydrochloride and sodium acetate in boiling aqueous-alcoholic solution. The *semicarbazone* of phenylacetyl*cyclo*pentane crystallised from alcohol in colourless needles, m. p. 117—118° (Found : N, 17·4. $C_{14}H_{19}ON_3$ requires N, 17·1%).

2-*Benzyl*cyclo*hexanol* (II). *cyclo*Hexene oxide (35 g.) was slowly added to an ice-cold Grignard reagent prepared from benzyl chloride (47·5 c.c.), magnesium turnings (10·5 g.), and anhydrous ether (250 c.c.). After removal of the flask from the ice-bath, the solution boiled spontaneously, and continued to boil for a while. When the reaction had subsided, the whole was refluxed for an hour, and the product decomposed with ammonium chloride solution. The washed ethereal solution was dried and distilled. The lower fractions were redistilled, and gave a fraction, b. p. 85—95°/25 mm. (10 g.), which appeared to be a mixture of stereoisomeric 2-chloro*cyclo*hexanols (see below). The carbinol fraction, b. p. 130°/5—6 mm., was recrystallised from ligroin, giving long colourless needles of 2-benzyl*cyclo*hexanol (34 g.), m. p. 76·5—77·5°, alone or mixed with a specimen prepared by reduction of 2-benzyl*cyclo*hexanone (Cook and Hewett, this vol., p. 69). The 3 : 5-*dinitrobenzoate* of 2-benzyl*cyclo*hexanol crystallised from alcohol in pale yellow, stout needles, m. p. 133—135° (Found : C, 62·4; H, 5·4. $C_{20}H_{20}O_6N_2$ requires C, 62·5; H, 5·25%). Oxidation of 2-benzyl*cyclo*hexanol with cold chromic acid, as described above, gave in good yield 2-benzyl*cyclo*hexanone, the semicarbazone of which had m. p. 168—169° alone or mixed with a specimen prepared from α-benzylpimelic acid (Cook and Hewett, *loc. cit.*).

2-*Chloro*cyclo*hexanol*. The fraction, b. p. 85—95°/25 mm., from the above preparation of 2-benzyl*cyclo*hexanol was treated with phenyl *iso*cyanate in light petroleum. After some days a heavy oil separated which slowly deposited crystals. These, recrystallised successively from alcohol and *cyclo*hexane (some carbanilide remained undissolved), had m. p. 89—90°, not depressed by a specimen of the phenylurethane of *trans*-2-chloro*cyclo*hexanol, m. p. 94—96° (Godchot, *Compt. rend.*, 1923, **176**, 448, gives m. p. 97—98°). The major portion of the phenylurethane was present in the non-crystalline fraction. This was distilled at 0·1 mm. (b. p. about 170°), and crystallised from ligroin, and then from *cyclo*hexane. The product, probably mainly the phenylurethane of *cis*-2-chloro*cyclo*hexanol, formed colourless crystals, m. p. 56—59° to a cloudy liquid. Contamination with a little of the higher-melting compound rendered complete purification impracticable.

2-*Phenyl*cyclo*hexanol*. *cyclo*Hexene oxide (49 g.) was added to an ice-cold solution of phenyl-lithium prepared from bromobenzene (50 c.c.), stout lithium wire (7·5 g.), and anhydrous ether (500 c.c.), the whole operation being conducted in an atmosphere of nitrogen (compare Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1932, **54**, 1957). After removal from the ice-bath, the solution boiled spontaneously for ½ hour. Boiling was continued for 2½ hours, and the whole was then kept at room temperature over-night, and decomposed with ice-water. Distillation gave a fraction, b. p. 60—80°/16 mm. (15 g.; mainly *cyclo*hexene oxide), and then 2-phenyl*cyclo*hexanol (63·3 g.), b. p. 153—154°/16 mm. This carbinol had m. p. 56—57° after crystallisation from light petroleum, and gave a phenylurethane, m. p. 137—138·5° (von Braun, Gruber, and Kirschbaum, *loc. cit.*, give 54—55°, and 138—139°, as the m. p.'s of 2-phenyl*cyclo*hexanol and its phenylurethane). The 3 : 5-*dinitrobenzoate* of 2-phenyl*cyclo*hexanol had m. p. 121—121·5° (from alcohol) (Found : C, 61·5; H, 4·9. $C_{19}H_{18}O_6N_2$ requires C, 61·6; H, 4·9%). Additional proof of the structure of the carbinol was afforded by its oxidation products (below).

*2-(1'-Naphthyl)*cyclo*hexanol.* *cyclo*Hexene oxide (49 g.) was slowly added to an ice-cold solution of 1-naphthyl-lithium prepared from 1-bromonaphthalene (103·5 g.), stout lithium wire (7·5 g.), and anhydrous ether (500 c.c.), the operations being conducted in an atmosphere of nitrogen. After addition of the oxide, the solution was kept in ice for ½ hour, then at room temperature for 1 hour, and was finally boiled for 15 hours. After decomposition with ice, the ethereal solution was washed, dried (sodium sulphate), and distilled. The carbinol fraction was redistilled, and the crystalline distillate (47·5 g., b. p. 183°/1 mm.) was recrystallised from alcohol. *2-(1'-Naphthyl)*cyclo*hexanol* formed colourless microscopic plates, m. p. 129—130° (Found: C, 84·7; H, 7·75. $C_{16}H_{18}O$ requires C, 84·9; H, 8·0%). Its 3 : *5-dinitrobenzoate* formed a primrose-yellow microcrystalline powder (from alcohol), m. p. 162—163° (Found: C, 65·6; H, 4·95. $C_{23}H_{20}O_6N_2$ requires C, 65·7; H, 4·8%), and its *phenylurethane* crystallised from *cyclo*hexane in colourless microscopic needles, m. p. 134—135° (Found: C, 79·3; H, 6·7. $C_{23}H_{23}O_2N$ requires C, 79·95; H, 6·7%).

The structure of this carbinol was established by its dehydration to 1-naphthyl-Δ^1-*cyclo*hexene, identical with a specimen prepared from 1-(1'-naphthyl)*cyclo*hexanol (Weiss and Woidich, *Monatsh.*, 1925, **46**, 456): A mixture of the carbinol (3 g.) and anhydrous zinc chloride (6 g.) was heated at 160—170° for 40 minutes, cooled, and extracted with benzene, and the benzene extract distilled. The distillate, b. p. 131°/0·4 mm., which absorbed a quantity of bromine corresponding with one double bond, was converted into the picrate, and this was recrystallised several times from methyl alcohol (m. p. 120—121·5°). The hydrocarbon regenerated from this picrate was distilled over sodium in a vacuum, and recrystallised from methyl alcohol; it then had m. p. 44°, not depressed by an authentic sample of 1'-naphthyl-Δ^1-*cyclo*hexene. Weiss and Woidich give m. p. 36° for this hydrocarbon, but our sample, prepared by their method, had m. p. 46° after crystallisation from methyl alcohol, and gave a picrate, m. p. 124·5—125·5°.

The same hydrocarbon resulted from an attempt to prepare the bromide by adding phosphorus tribromide (10 g.) during 20 minutes to a suspension of 2-(1'-naphthyl)*cyclo*hexanol (24·4 g.) in carbon tetrachloride (25 c.c.), cooled in a freezing mixture. After being kept at room temperature over-night, the reaction mixture was decomposed with water, and the carbon tetrachloride solution was washed and distilled. The product, b. p. 166°/0·3 mm. (12 g.), contained some unaltered carbinol, which separated when a solution in light petroleum was cooled in a freezing mixture. The redistilled hydrocarbon (Found: C, 90·7; H, 7·9%) was purified through its picrate and crystallised from methyl alcohol; it then had m. p. 44°, not depressed by an authentic specimen of the *cyclo*hexene.

*Hydrophenanthrene Derivatives.—2-Phenyl*cyclo*hexanone.* A solution of chromic acid (33 g.) in 80% acetic acid (65 c.c.) was added dropwise to a stirred solution of 2-phenyl*cyclo*hexanol (56·5 g.) in glacial acetic acid (625 c.c.). After being kept at room temperature over-night, the acetic acid was removed in a vacuum, and the residue extracted with water and ether. The ethereal extract was washed with sodium carbonate solution, giving 9·6 g. of δ-benzoylvaleric acid, m. p. 75—76° (from *cyclo*hexane) (Found: C, 69·8; H, 6·9. Calc.: C, 69·9; H, 6·8%). The semicarbazone had m. p. 183—185° (Auwers and Treppmann, *Ber.*, 1915, **48**, 1217, give 77—78° and 187°, as the m. p.'s of this acid and its semicarbazone).

The neutral ethereal solution of the oxidation products was dried and distilled, yielding 32·7 g. of 2-phenyl*cyclo*hexanone (b. p. 160°/16 mm.). This ketone had m. p. 50—53° after crystallisation from light petroleum, and gave an oxime and a semicarbazone having the m. p.'s recorded by von Braun, Gruber, and Kirschbaum (*loc. cit.*).

*Ethyl 2-phenyl*cyclo*hexanol-1-acetate* (III). A mixture of 2-phenyl*cyclo*hexanone (32·7 g.), ethyl bromoacetate (33·6 g.), dry zinc filings (purified by washing first with warm alkali and then with alcohol and ether; 13·6 g.), and pure benzene (100 c.c.) was warmed on the water-bath until a reaction set in. The vigorous reaction caused the mixture to boil for 10 minutes without external heating. When this had subsided, the whole was boiled for ½ hour, and the product decomposed with ice-cold dilute sulphuric acid, washed, dried, and distilled. The *hydroxy-ester* (III) (34 g., 70% yield) had b. p. 146—154°/0·8 mm., and was shown by analysis to have undergone partial dehydration (Found: C, 75·4; H, 8·4. $C_{16}H_{22}O_3$ requires C, 73·25; H, 8·5%). The *hydroxy-acid* (corresponding with III) was obtained by hydrolysis, and crystallised from water in small colourless needles, m. p. 128—129° (Found: C, 71·5; H, 7·6. $C_{14}H_{18}O_3$ requires C, 71·7; H, 7·8%).

*Ethyl 2-phenyl-Δ^1-*cyclo*hexenylacetate.* Thionyl chloride (16·9 g.) was added slowly to a well-stirred ice-cold mixture of the foregoing hydroxy-ester (34 g.), anhydrous ether (60 c.c.), and pure pyridine (28·6 c.c.). Stirring and cooling were continued for 2 hours, the solution was

then poured into water, and the ethereal solution was washed, dried, and distilled. *Ethyl 2-phenyl-Δ^1-cyclohexenylacetate* (27·4 g.) formed a colourless liquid, b. p. 123—125°/0·8 mm. (Found : C, 78·2; H, 8·2. $C_{16}H_{20}O_2$ requires C, 78·6; H, 8·3%). Hydrolysis with boiling aqueous-alcoholic potash gave *2-phenyl-Δ^1-cyclohexenylacetic acid*, a gum, b. p. 150—155°/0·4 mm., which slowly crystallised. After crystallisation from ligroin this acid formed colourless rhombs, m. p. 92·5—93·5° (Found : C, 78·1; H, 7·6. $C_{14}H_{16}O_2$ requires C, 77·7; H, 7·5%).

2-Phenylcyclohexylacetic Acid (IV). The distilled, but not recrystallised, unsaturated acid (17·5 g.) was hydrogenated in acetic acid solution, a palladium-black catalyst being used. The resulting *2-phenylcyclohexylacetic acid* (12·4 g.) crystallised from aqueous acetic acid in conglomerates of colourless needles, m. p. 168—170° (Found : C, 76·9; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). The liquors contained a lower-melting acid, but this could not be isolated in the pure state. When, however, a fraction, m. p. 65—85° (about 2 g.), was dehydrated with concentrated sulphuric acid (20 c.c.) at 100°, and the product crystallised from light petroleum, there was formed a *ketone* (0·5 g.), m. p. 95—96° (Found : C, 84·0; H, 8·1. $C_{14}H_{16}O$ requires C, 83·95; H, 8·1%), which gave an *oxime*, m. p. 175—177° (Found : C, 78·6; H, 7·9. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0%). This ketone is probably stereoisomeric with the hexahydrophenanthrone (V) obtained by dehydration of the above acid of m. p. 168—170°.

Stereoisomeric 2-phenylcyclohexylacetic acid (?).* A solution of 2-phenyl*cyclo*hexanol (17·6 g.) in carbon tetrachloride (25 c.c.) was added during 2 hours with stirring to phosphorus tribromide (13·6 g.), cooled in a freezing mixture. The mixture was stirred at 15° for another hour, and the bromo-compound, b. p. 150—155°/16 mm. (4·8 g.), was isolated in the usual way. This was added to the potassio-compound from ethyl malonate (7·2 g.) and potassium (1·2 g.) in benzene (15 c.c.), and the whole was heated on the water-bath for 4 days. The product was decomposed with water, and the benzene solution dried and distilled. The fraction, b. p. 120—150°/1 mm. (3·1 g.), was hydrolysed with aqueous-alcoholic potash, the acidic product heated at 200° in order to effect decarboxylation of the substitnted malonic acid, and the resulting *2-phenylcyclohexylacetic acid* crystallised from water. It formed small colourless plates, m. p. 84—85°. The yield was only 0·1 g. (Found : C, 77·1; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%).

9-Keto-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (hexahydrophenanthrone) (V). (a) A mixture of 2-phenyl*cyclo*hexylacetic acid (m. p. 168—170°) (1·5 g.) and thionyl chloride (5 c.c.) was refluxed for an hour, the excess of thionyl chloride removed in a vacuum, and the residual acid chloride dissolved in carbon disulphide (7·5 c.c.) and treated at 0° with anhydrous aluminium chloride (1 g.). After being kept in the ice-bath for ¼ hour, the whole was heated to boiling and then decomposed with ice and hydrochloric acid. The ketone (0·8 g.), b. p. 132—135°/0·5 mm., was identical with that obtained by dehydration with sulphuric acid.

(b) A solution of 2-phenyl*cyclo*hexylacetic acid (9·5 g.) in concentrated sulphuric acid (47·5 c.c.) was heated on the water-bath for 10 minutes, cooled, and poured on ice. The ketone was extracted with ether, washed with dilute sodium carbonate solution, and distilled. *9-Keto-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene* (6·3 g.) formed a colourless syrup, b. p. 137—138°/0·5 mm. (Found : C, 83·8; H, 8·0. $C_{14}H_{16}O$ requires C, 83·95; H, 8·1%). The *semicarbazone* formed a colourless crystalline powder (from alcohol), m. p. 195—196° (Found : C, 70·5; H, 7·4. $C_{15}H_{19}ON_3$ requires C, 70·3; H, 7·1%), and the *oxime*, obtained by 3 hours' heating at 100° with hydroxylamine hydrochloride in anhydrous pyridine, crystallised from methyl alcohol in colourless needles, m. p. 123·5—124·5° (Found : C, 77·75; H, 8·1. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0%).

9-Hydroxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene. A solution of the ketone (V) (4 g.) in ethyl alcohol (40 c.c.) was hydrogenated, Adams's platinum oxide catalyst (0·5 g.) being used. The resulting *carbinol* was crystallised from *cyclo*hexane and then light petroleum, forming soft colourless needles (2·6 g.), m. p. 114—115° (Found : C, 82·8; H, 8·75. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%). Dehydrogenation with platinum-black at 310—320° (4 hours) gave 9-phenanthrol, m. p. 151—152° (*lit.*, 152°) after purification through its picrate, m. p. 182—184° (*lit.*, 183°). A more soluble picrate, probably of phenanthrene, was also present in the crude product.

Hexahydrophenanthrene. Octahydrophenanthrol (2·5 g.) was heated at 180° for 20 minutes with anhydrous zinc chloride (5 g.), and the resulting *hexahydrophenanthrene* (1·5 g.) distilled over sodium. It had b. p. 125—126°/2·5 mm. and $n_D^{14·5°}$ 1·5810 (Found : C, 90·95; H, 9·0.

* (Added in proof) The same structure (IV) is ascribed by Ghose (*Science and Culture*, 1935, 1, 299) to an acid, m. p. 69—70°, prepared by another method, with the avowed intention of converting it into a phenanthrene derivative.

$C_{14}H_{18}$ requires C, 91·3; H, 8·7%). Dehydrogenation of this hydrocarbon with platinum-black at 300° (2 hours) gave phenanthrene, identified by mixed m. p.'s of the hydrocarbon and its picrate with authentic specimens.

Oxidation of as.-*octahydrophenanthrene.* A solution of chromic acid (30 g.) in 80% acetic acid (60 c.c.) was added during an hour to a well-stirred solution of *as.*-octahydrophenanthrene (prepared by aluminium chloride cyclisation of β-phenylethyl-Δ^1-*cyclo*hexene) (25 g.) in glacial acetic acid (250 c.c.). After 4 days at room temperature, *iso*propyl alcohol was added to destroy excess of chromic acid, and the acetic acid was removed on the water-bath under reduced pressure. The residue was extracted with water and ether, and the ethereal extract was washed successively with dilute sulphuric acid, dilute sodium carbonate solution, and water. The dried solution was fractionated. The highest-boiling fraction (6·8 g.), b. p. 100—130°/0·2 mm., was treated with Girard's ketonic reagent, and the ketonic products regenerated from the aqueous extract by means of hydrochloric acid (details of procedure as given in J., 1935, 1323). The resulting ketone mixture formed a thick yellowish liquid (4·5 g.), which, after distillation at 0·1 mm., was heated on the water-bath for 3 hours with hydroxylamine hydrochloride (4·4 g.) in anhydrous pyridine (20 c.c.). The resulting mixture of oximes was fractionally crystallised from alcohol, giving a sparingly soluble *oxime* (0·35 g.), which formed long colourless needles, m. p. 186·5—187·5°, and depressed the m. p. of the oxime, m. p. 175—177°, of one of the stereoisomeric hexahydrophenanthrones (Found: C, 78·8, 78·5; H, 7·4, 6·95; N, 7·0. $C_{14}H_{15}ON$ requires C, 78·8; H, 7·1; N, 6·6%. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0; N, 6·5%). The more soluble oxime (1·5 g.) was recrystallised from aqueous alcohol; it then had m. p. 119—121°, not depressed by the oxime, m. p. 124°, of hexahydrophenanthrone (V). This oxime was hydrolysed, and the ketone converted into its semicarbazone, which had m. p. 191—196°, not depressed by the semicarbazone, m. p. 195—196°, of hexahydrophenanthrene.

Hexahydroanthrones.—2-Benzylhexahydrobenzoic acids (VII). (a) Thionyl chloride (11·5 c.c.) was added dropwise to an ice-cold mixture of 2-benzyl*cyclo*hexanol (27·7 g.) and dimethylaniline (20 c.c.). The whole was then heated on the water-bath until liberation of sulphur dioxide ceased; water was added and the product was extracted with ether, washed, and distilled, giving a colourless liquid (22·2 g.), b. p. 85—100°/0·2 mm. (Found: C, 80·35; H, 8·8. $C_{13}H_{17}Cl$ requires C, 74·8; H, 8·2%). This chloro-compound was therefore contaminated with much hydrocarbon, and even worse results were obtained when pyridine was used in place of dimethylaniline.

A Grignard solution was prepared from this chloro-compound (20 g.) and magnesium turnings (2·4 g.) in anhydrous ether (100 c.c.), methylmagnesium iodide being required for activation. Dry carbon dioxide was passed into the ice-cold solution for 3 hours, the product was decomposed with dilute hydrochloric acid, and acidic substances were extracted by sodium carbonate solution. The crude resinous acids (isolated by means of ether) were dissolved in ligroin, and the solution kept in the refrigerator for several hours. 3·6 G. of a colourless powder separated, a further 0·45 g. being obtained by concentrating the mother-liquor and adding light petroleum. By fractional crystallisation from ligroin and light petroleum, this mixture was separated into *2-benzylhexahydrobenzoic acid* (VII), m. p. 133—134°, provisionally denoted as the *trans*-acid, which separated from *cyclo*hexane in colourless microscopic crystals (Found: C, 77·2; H, 8·4. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%), and a *stereoisomeride*, provisionally regarded as *cis*-2-benzylhexahydrobenzoic acid, which separated from light petroleum as a colourless crystalline powder, m. p. 86—88°, although the resulting cloudy liquid was not completely clear below 94° (Found: C, 77·3; H, 8·2%).

(b) Phosphorus tribromide (5 c.c.) was added dropwise during 20 minutes to an agitated suspension of 2-benzyl*cyclo*hexanol (28·5 g.) in carbon tetrachloride (25 c.c.), cooled in a freezing mixture. The mixture was kept in the freezing mixture for an hour and then over-night at room temperature. The resulting *1-bromo-2-benzyl*cyclo*hexane* (16·5 g.; 44% yield), isolated in the usual manner, formed a colourless refractive liquid, b. p. 120°/0·4 mm. (Found: C, 62·5; H, 7·0. $C_{13}H_{17}Br$ requires C, 61·7; H, 6·8%). 6 G. of carbinol were recovered by hydrolysis of the phosphite esters.

An ice-cold Grignard solution prepared from this bromo-compound (16 g.), magnesium turnings (1·55 g.), and anhydrous ether (80 c.c.) was treated with ethyl chloroformate (6·9 g.), diluted with ether (15 c.c.). After being kept in the ice-bath for ½ hour and then at room temperature over-night, the product was treated with ammonium chloride solution, and the ethereal solution was washed, dried, and distilled. The fraction, b. p. 120—130°/0·2—0·3 mm. (6·25 g.), was hydrolysed with boiling aqueons-alcoholic potash, and the resulting mixture of acids was fractionally crystallised from ligroin (fractions I and II) and light petroleum (fraction

III) into three fractions: I, m. p. 133—134° (1·45 g.); II, m. p. 138—140° after sintering (0·55 g.); III, m. p. 102—113° (0·75 g.). Fraction I, after crystallisation, had m. p. 133—134·5°, and was shown to be identical with *trans*-2-benzylhexahydrobenzoic acid (VII). Fraction II crystallised from *cyclo*hexane in colourless leaflets, m. p. 140—141°, and depressed the m. p. of the acid from fraction I (Found: C, 77·0; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). This *acid* is provisionally regarded as 4-benzylhexahydrobenzoic acid, formed by migration. Diazomethane gave a methyl ester, m. p. 33°. Fraction III seemed to be a mixture of these two acids, but no pure compound could be isolated. The residue from the distillation of the mixture of esters from the Grignard reaction crystallised from xylene, and then from benzene, in colourless crystals, m. p. 180—181° to a cloudy liquid, clear at 191°. This was apparently 2 : 2'-*dibenzyl*-*di*cyclo*hexyl*, probably not stereochemically homogeneous (Found: C, 90·2; H, 9·9. $C_{26}H_{34}$ requires C, 90·1; H, 9·9%).

(c) Sodium (16·6 g.) was gradually added to a boiling solution of *o*-benzylbenzoic acid (Barnett, Cook, and Nixon, J., 1927, 508) (5 g.) in amyl alcohol (200 c.c.). After the sodium had dissolved, the solution was poured into water and the amyl alcohol was removed in steam. Most of the alkali was neutralised, the solution filtered, and the filtrate acidified. The acidic product was dried in ethereal solution and recrystallised from ligroin. The crystals (3·3 g.) had m. p. 121—125°, raised by recrystallisation from *cyclo*hexane and then ligroin to 133—134°. This m. p. was not depressed by *trans*-2-benzylhexahydrobenzoic acid prepared from 2-benzyl*cyclo*hexanol. This method of preparation supports the *trans*-configuration.

trans-*Hexahydroanthrone* (VIII). (a) *trans*-2-Benzylhexahydrobenzoic acid (1·5 g.) was submitted to an internal Friedel–Crafts reaction exactly as in the case of 2-phenyl*cyclo*hexylacetic acid (p. 77). After removal of the carbon disulphide, crystallisation from alcohol gave 0·8 g. of trans-*hexahydroanthrone*, which formed colourless prisms, m. p. 109—109·5° (Found: C, 83·9; H, 8·2. $C_{14}H_{16}O$ requires C, 83·95; H, 8·1%). Dehydrogenation of this ketone (0·1 g.) with platinum-black (50 mg.) at 300° gave, after crystallisation from benzene, colourless leaflets, m. p. 205—207°, not depressed by anthracene. Without further purification this was oxidised with sodium dichromate in boiling acetic acid, and gave anthraquinone, identified by mixed m. p., and by the anthraquinol reaction with zinc dust and alkali.

(b) Dehydration of *trans*-2-benzylhexahydrobenzoic acid (0·4 g.) by concentrated sulphuric acid (2 c.c.) at 100° (10 minutes) gave the same hexahydroanthrone (0·25 g.), m. p. 109°. It was subsequently found that heating is unnecessary; as soon as the acid has dissolved in cold concentrated sulphuric acid dehydration is complete. This ketone was hardly affected by hydroxylamine in boiling aqueous-alcoholic solution (2 hours), but gave an *oxime* when heated on the water-bath with hydroxylamine hydrochloride (1 part) in anhydrous pyridine (10 parts) for 4 hours.* The oxime separated from *cyclo*hexane as a colourless crystalline powder, m. p. 174·5—175·5° (Found: C, 78·1; H, 7·8. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0%).

cis-*Hexahydroanthrone* (VIII). (a) A solution of *cis*-2-benzylhexahydrobenzoic acid, m. p. 86—88° (1 g.), in concentrated sulphuric acid (5 c.c.) was heated on the water-bath for 5 minutes. The resulting mixture of ketones (0·9 g.) was fractionally crystallised from alcohol. There was isolated 0·15 g. of the pure *trans*-ketone, m. p. 109°. The more soluble fractions yielded 0·4 g. of cis-*hexahydroanthrone*, which crystallised from aqueous alcohol in colourless needles, m. p. 79—80°. The resulting cloudy liquid became clear only at 85°, so a little of the *trans*-ketone was probably still present (Found: C, 84·0; H, 7·9. $C_{14}H_{16}O$ requires C, 83·95; H, 8·1%). The *oxime* of the *cis*-ketone, prepared by the pyridine method, crystallised from ligroin in clusters of colourless needles, m. p. 150—151° (Found: C, 78·2; H, 7·9. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0%). Dehydrogenation of *cis*-hexahydroanthrone with platinum-black gave anthracene, m. p. 209—211°, oxidised to anthraquinone, m. p. 275°.

(b) When the crude acid, m. p. 121—125° (5 g.), obtained by reduction of *o*-benzylbenzoic acid with sodium and amyl alcohol, was dehydrated with concentrated sulphuric acid (5 minutes at 100°), and the product recrystallised twice from alcohol, pure *trans*-hexahydroanthrone (1·05 g.), m. p. 109°, was obtained. The liquor from the final crystallisation gave, on dilution with water, 1·05 g. of almost pure *cis*-hexahydroanthrone, m. p. 79—80° (clear at 87°). Evidently a mixture of the two anthrones arises from either *cis*- or *trans*-benzylhexahydrobenzoic acid, and this method appears to furnish the simplest route to both hexahydroanthrones. Only the *trans*-ketone was obtained by dehydration with cold sulphuric acid.

ω-cyclo*Hexyl-o-toluic acid* (IX). A solution of *o*-benzylbenzoic acid (8 g.) in glacial acetic acid (100 c.c.) was shaken with hydrogen in the presence of Adams's platinum oxide catalyst

* We are indebted to Dr. W. E. Bachmann for bringing to our notice this method of oximation.

(1·2 g.). In 10½ hours 2·6 l. of hydrogen were absorbed, corresponding with 6 atoms. The acetic acid was removed under reduced pressure and the residue was recrystallised from light petroleum; it then had m. p. 88—93°. This product was contaminated with a little o-benzylbenzoic acid, and for purification, a solution of the acid (4 g.) in concentrated sulphuric acid (20 c.c.) was kept at room temperature for ½ hour and then poured into water. The precipitate was digested with cold dilute sodium carbonate solution, which dissolved the desired acid, leaving a residue of anthrone. ω-cyclo*Hexyl*-o-*toluic acid* (IX) crystallised from light petroleum in colourless plates, m. p. 95·5—96·5°, and did not absorb bromine or reduce cold alkaline permanganate (Found: C, 77·2; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%).

A 5% solution of potassium permanganate (3·5 g.) was added during 1 hour to a boiling solution of this acid (1 g.) in dilute alkali. The filtered solution was acidified and extracted with ether repeatedly. The ethereal extract was dried, and the ether removed. The residual gum gave a white solid when digested with benzene, and from this, phthalic anhydride (identified by mixed m. p.) was obtained by sublimation under reduced pressure.

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The Research Institute of The Cancer Hospital (Free),
London, S.W. 3. [*Received, November 30th*, 1935.]

Note by R. Robinson.—Dr. Fulton and I are glad to have the opportunity of confirming the view of the course of the reaction between β-phenylethylmagnesium bromide and *cyclo*hexene oxide put forward in the present communication (p. 72).

*cyclo*Pentylformaldehyde, prepared according to the method of Clemo and Ormston (J., 1933, 362), which is based on that of Bedos (*Compt. rend.*, 1929, **189**, 255), reacted with β-phenylethylmagnesium bromide in ethereal solution with formation of β-phenylethyl*cyclo*pentylcarbinol in excellent yield. The alcohol had the properties previously attributed to 2-β-phenylethyl-*cyclo*hexanol (Fulton and Robinson, *loc. cit.*) and it solidified completely in a freezing mixture. Definite identification was effected through the semicarbazone of the related ketone, which had m. p. 157°, alone or mixed with the specimen made in stages from *cyclo*hexene oxide. The recognition that the reaction involves rearrangement implicates other substances as follows. The *p*-nitrobenzoate and the chloride are β-phenylethyl*cyclo*pentylcarbinyl derivatives; for "2-β-phenylethyl*cyclo*hexanone" read β-*phenylethyl* cyclo*pentyl ketone*; for "2-β-phenylethyl-1-ethyl*cyclo*hexanol" read β-*phenylethyl*cyclo*pentylethylcarbinol*.

The hydrocarbons described are of uncertain constitution: the supposed 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene solidified at − 11° to − 12° and was therefore probably homogeneous; it should be 1-cyclo*pentylhydrindene*, and the formation of phenanthrene on heating with sulphur was due to rearrangement. The supposed 2-β-phenylethyl-1-ethyl-Δ¹-*cyclo*hexene is now best described as a *hydrocarbon*, $C_{16}H_{22}$, and the supposed ethyloctahydrophenanthrene, which gave both phenanthrene and anthracene on heating with sulphur, is now also to be regarded as a *hydrocarbon*, $C_{16}H_{22}$. Incidentally the apparent clash with the results of Bardhan and Sengupta (J., 1932, 2520) no longer exists.—The Dyson Perrins Laboratory, Oxford University. [*Received, December 12th*, 1935.]

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17. *Aconitine. Part I. Oxonitin and the Oxidation of Aconitine with Nitric Acid and Chromic Acid.*

By Alexander Lawson.

Oxonitin, one of the only two previously described oxidation products of aconitine, has now been known for 25 years, but its formula is still undecided. The original C_{23} formula of Carr (J., 1912, **101**, 2241) and those of Brady (J., 1913, **103**, 1821), Barger and Field (J., 1915, **107**, 231), and Majima and Suginome (*Ber.*, 1925, **58**, 2047) were recognised by Späth and Galinovsky (*Ber.*, 1930, **63**, 2994) and Henry and Sharp (J., 1931, 581) to be too small. Whilst, however, Späth and Galinovsky proposed $C_{32}H_{43}O_{12}N$, Henry and Sharp preferred $C_{31}H_{39}O_{12}N$, and were supported in this by further observations of Majima and co-workers (*Ber.*, 1932, **65**, 595), the question turning on whether the molecule did or did not contain a methylimide group.

Späth and Galinovsky (*Ber.*, 1931, **64**, 2201) pointed out that failure to obtain the theoretical quantity of silver iodide in the methylimide determination might not indicate the absence of such a group and instanced other similar cases. They pointed out that, on the C_{32} formula, the liberation of acetaldehyde in this oxidation noted by Carr would imply that the methylimide group remained unaffected.

The analytical results now presented, obtained with oxonitin prepared in this laboratory, are in agreement with the formula of Späth and Galinovsky. No more than traces of silver iodide, however, could be obtained in the methylimide determination. It would appear, therefore, that the evidence for the presence of this group is somewhat scanty, and that, in view of the poor yields of oxonitin obtained by Carr, the acetaldehyde need not be a product of the oxonitin oxidation in particular, and should therefore not be admitted as evidence in the question under consideration.

Oxonitin oxidised with nitric acid in acetic acid solution has been shown to yield a crystalline acidic *compound* with the loss of a methoxyl group. To the compound, which gives Liebermann's nitroso-reaction, and probably contains a nitro-group in addition, the formula $C_{31}H_{35}O_{14}N_3$ has been ascribed.

By the action of chromic acid on aconine, Schulze (*Arch. Pharm.*, 1908, **246**, 281) obtained a base, $C_{24}H_{35}O_8N$, and a substance, $C_{24}H_{33}O_9N$, with amphoteric properties. A base, $C_{30}H_{37}O_9N$, for which the name *aconitoline* is proposed, has now been obtained by the action of chromic acid on aconitine dissolved in acetone. It contains one methoxyl and two hydroxyl groups less than the parent alkaloid, and would therefore appear to be derived by the oxidation of some other part of the molecule than that concerned in the oxonitin oxidation. Attempts to acetylate the remaining hydroxyl group were unsuccessful, the initial material being unchanged. The formula of aconitoline may be extended thus:

$$C_{17}H_{16}O(CH_3\cdot CO\cdot O)(C_6H_5\cdot CO\cdot O)(N\cdot CH_3)(OH)(O\cdot CH_3)_3.$$

In view of the difficulty of isolating the hydrolysis product of aconitine on account of its great solubility in water, it was thought desirable to try the action of hydrolysing agents on aconitoline. By the action of sodium ethoxide, benzoic acid was split off, leaving a hygroscopic base, $C_{23}H_{33}O_8N$; this could be readily crystallised as the *hydrochloride*, $C_{23}H_{33}O_8N,HCl,3H_2O$, the water of crystallisation of which was not removable below 150°. Prolonged heating with sodium ethoxide did not further hydrolyse this compound. The base on acetylation yielded a crystalline *diacetyl* derivative, showing the presence of two hydroxyl groups.

By the action of dilute nitric acid on aconitine, a crystalline *acid*, $C_{31}H_{35}O_{13}N_3$, containing a nitroso-group was obtained. The formula may be extended thus: $C_{18}H_{16}N(O\cdot CH_3)_3(NO_2)(NO)(C_6H_5\cdot CO\cdot O)(CH_3\cdot CO\cdot O)(CO\cdot OH)(OH)$. The acid contains three of the four methoxyl and one of the three hydroxyl groups present in the aconitine molecule, the methylimide group also having been lost. In view of the similarity in formula of this compound and the product obtained by the action of nitric acid on oxonitin, the oxonitin oxidation and that of aconitine with nitric acid may be concerned with the same part of the molecule.

By the action of anhydrous hydrogen chloride on a suspension of the nitroso-acid in alcohol, the nitroso-group was removed, yielding a crystalline *hydrochloride* of an amino-acid, $C_{31}H_{36}O_{12}N_2,HCl,2H_2O$.

By the hydrolysis of the nitroso-acid $C_{31}H_{35}O_{13}N_3$ with alcoholic barium hydroxide (compare Majima and Suginome, *loc. cit.*), benzoic and acetic acids were removed, giving the water-soluble *derivative* $C_{22}H_{29}O_{11}N_3$.

Aconitoline, oxidised with nitric acid under the same conditions as aconitine, yielded a corresponding *nitroso-acid*, $C_{29}H_{33}O_{13}N_3$, the methylimide group having been lost. With anhydrous hydrogen chloride the nitroso-group could be removed, giving an *amino-acid* $C_{29}H_{34}O_{12}N_2$, which yielded, on hydrolysis of the benzoyl group with sodium ethoxide, the crystalline *hydrochloride* of an amino-acid $C_{22}H_{30}O_{11}N_2$. The free amino-acid was not obtained crystalline.

By the action of nitrous acid on aconitine dissolved in acetic acid, a crystalline *nitroso-compound*, $C_{31}H_{40}O_{12}N_2$, was obtained in rather poor yield.

The preparation of the derivatives described above facilitates the characterisation of the three oxidation products, oxonitin, aconitoline, and the nitroso-acid. Although no deep-seated decomposition products of the aconitine molecule have been obtained, the formation of the nitro-nitroso-derivative may possibly indicate the presence of a tetrahydroquinoline system in the molecule.

Experimental.

Oxonitin was prepared by Barger and Field's method (*loc. cit.*), except that no acetic acid was used to keep the acetone neutral during the oxidation; the yield from 5 g. of aconitine was 2·4 g., m. p. 278° (decomp.) (Found: C, 60·9, 60·6, 60·8, 61·1; H, 6·85, 6·8, 6·9, 6·7; N, 2·5, 2·3, 2·2, 2·2; OMe, 19·7, 19·8. Calc. for $C_{32}H_{43}O_{12}N$: C, 60·6; H, 6·8; N, 2·2; 4OMe, 19·6%).

Oxidation of Oxonitin with Nitric Acid.—Oxonitin (1 g.), suspended in glacial acetic acid (5 c.c.), dissolved when heated with concentrated nitric acid (5 c.c.) on the steam-bath. After brown fumes ceased to be evolved, the product was poured into water, collected, and crystallised from alcohol–acetone, forming stout, pale yellow prisms, m. p. 263° (decomp.) (Found: C, 55·3, 55·5; H, 5·4, 5·4; N, 6·1, 6·0; OMe, 13·4; NMe, nil. $C_{31}H_{35}O_{14}N_3$ requires C, 55·3; H, 5·2; N, 6·2; 3OMe, 13·8%).

Aconitoline.—Aconitine (5 g.) was dissolved in purified acetone (50 c.c.) and chromic acid (5 g.), dissolved in acetone (50 c.c.), was added. After 3 days the acetone was allowed to evaporate and the residue was dissolved in sulphurous acid. The solution was shaken with ether to remove a neutral substance, made alkaline with sodium carbonate, and extracted with ether; evaporation of the ether left a syrup, which crystallised from alcohol in prisms (2·3 g.), m. p. 220° (Found: C, 64·6, 65·1, 64·5, 65·0; H, 6·8, 6·8, 6·8, 6·8; N, 2·5, 2·5, 2·7, 2·6; OMe, 15·15, 15·4; NMe, 5·0; active H, 0·179, 0·198. $C_{30}H_{37}O_9N$ requires C, 64·9; H, 6·85; N, 2·5; 3OMe, 16·7; NMe, 5·4%; 1 active H, 0·180). *Aconitoline* was much less stable to alkaline potassium permanganate than the parent alkaloid.

Hydrolysis of Aconitoline.—Four times the theoretical amount of sodium ethoxide in ethyl alcohol was added to an alcoholic solution of aconitoline, and the mixture warmed for a few minutes on the water-bath. The solution was neutralised with dilute hydrochloric acid, the sodium chloride removed, the filtrate evaporated under reduced pressure, and the residue dissolved in water and extracted with ether to remove benzoic acid. On evaporation under reduced pressure, the product separated in fine needles, which were recrystallised from aqueous alcohol; m. p. 222° (Found: C, 51·5; H, 7·5; N, 2·4; Cl, 6·4; no loss in a vacuum at 100°. $C_{23}H_{33}O_8N,HCl,3H_2O$ requires C, 50·9; H, 7·4; N, 2·6; Cl, 6·55%). The free base could not be obtained crystalline; it distilled unchanged in a high vacuum. When it was heated with hydrochloric acid, the acetyl group was removed, but no crystalline product could be isolated. The base on treatment with acetic anhydride and sulphuric acid gave a *diacetyl* derivative crystallising in needles, m. p. 239° (Found: C, 60·25; H, 6·9; N, 2·5. $C_{27}H_{37}O_{10}N$ requires C, 60·6; H, 6·9; N, 2·6%).

Oxidation of Aconitine with Nitric Acid.—A mixture of nitric acid (50 c.c., *d* 1·2) and aconitine (5 g.) was heated under reflux on the steam-bath till brown fumes ceased to be evolved and the substance which separated had become crystalline (2 hours). Water (200 c.c.) was then added, and the product (3·4 g.) collected; it crystallised from alcohol–acetone in pale yellow prisms, m. p. 268° (decomp.) (Found: C, 56·4, 56·35; H, 5·4, 5·4; N, 6·45, 6·3; OMe, 13·0; NMe, nil. $C_{31}H_{35}O_{13}N_3$ requires C, 56·6; H, 5·4; N, 6·4; 3OMe, 14·15%). The *acid* gave the Liebermann nitroso-reaction, dissolved in alkali to give a brown solution, and was precipitated again by acid.

Hydrolysis of the Acid $C_{31}H_{35}O_{13}N_3$.—The acid (1 g.) was suspended in alcohol (25 c.c.), 0·25*N*-barium hydroxide (40 c.c.) added, and the mixture warmed for 30 minutes. Carbon dioxide was then passed through the clear solution to precipitate barium and the alcohol was removed by distillation under reduced pressure. Barium carbonate was removed and the filtrate was neutralised with dilute sulphuric acid, filtered, extracted with ether to remove benzoic acid, and evaporated almost to dryness on the water-bath under reduced pressure. On further concentration in a desiccator, the solution deposited crystals which, on recrystallisation from alcohol, gave very pale yellow prisms, m. p. 201° after softening at 186° (Found: C, 51·9, 51·2; H, 6·05, 5·8; N, 7·9; OMe, 19·5, 18·6; CO_2H, 8·2, 8·4. $C_{22}H_{29}O_{11}N_3$ requires C, 51·7; H, 5·7; N, 8·2; 3OMe, 18·2; CO_2H, 8·8%).

Action of Hydrogen Chloride on the Acid $C_{31}H_{35}O_{13}N_3$.—When anhydrous hydrogen chloride was bubbled through a suspension of the nitroso-acid (0·5 g.) in absolute alcohol (10 c.c.), the latter dissolved and a product separated which on recrystallisation from aqueous alcohol

formed yellow prisms, m. p. 218° (decomp.). The *substance* was soluble in water and gave the test for chloride, but not the Liebermann nitroso-reaction (Found: C, 52·8; H, 6·0; N, 3·7; Cl, 4·9. $C_{31}H_{36}O_{12}N_2$,HCl,$2H_2O$ requires C, 53·1; H, 5·85; N, 4·0; Cl, 5·1%). The free amino-acid, precipitated from an aqueous solution of the substance by sodium acetate, crystallised with some difficulty from alcohol in pale yellow rosettes, m. p. 207° (decomp.).

Action of Nitric Acid on Aconitoline.—When nitric acid (*d* 1·2) reacted with aconitoline under the conditions used for the corresponding oxidation of aconitine, a *nitroso-acid* separated, and on recrystallisation from alcohol–acetone, pale yellow prisms were obtained, m. p. 186° (decomp.) (Found: C, 55·7, 55·4; H, 5·4, 5·6; N, 6·2, 6·3; NMe, nil. $C_{29}H_{33}O_{13}N_3$ requires C, 55·15; H, 5·2; N, 6·65%).

By the action of anhydrous hydrogen chloride on this compound suspended in absolute alcohol, the nitroso-group was removed, and an amino-acid hydrochloride, m. p. 214° (decomp.), was isolated. The action of sodium acetate on this gave the *amino-acid*, which crystallised from aqueous alcohol in yellow prisms, m. p. 250° (decomp.) (Found: C, 58·9; H, 5·8; N, 4·8. $C_{29}H_{34}O_{12}N_2$ requires C, 57·8; H, 5·65; N, 4·65%).

Hydrolysis of the Amino-acid $C_{29}H_{34}O_{12}N_2$.—The acid was suspended in alcohol and warmed with four times the theoretical quantity of sodium ethoxide. When worked up in the manner previously described, the *hydrochloride* of the hydrolysed amino-acid was obtained in colourless felted needles from aqueous alcohol, m. p. 218° (decomp., after softening at 180°) (Found: C, 47·8; H, 6·2; N, 4·8; Cl, 6·3. $C_{22}H_{30}O_{11}N_2$,HCl,H_2O requires C, 47·7; H, 6·0; N, 5·1; Cl, 6·4%).

Oxidation of Aconitine with Nitrous Acid.—A solution of aconitine (1 g.) in aqueous acetic acid (50 c.c.) was heated on the water-bath, and saturated aqueous sodium nitrite slowly added till no more solid separated. The product, recrystallised from boiling acetic acid, formed small colourless prisms, m. p. 276° (decomp.), very sparingly soluble in the usual solvents. The *substance* gave the nitroso-reaction, but it was not found possible to remove this group with hydrogen chloride as in previous cases (Found: C, 58·8, 59·2, 58·5, 59·3; H, 6·35, 6·5, 6·3, 6·7; N, 4·2, 4·6, 4·4, 4·6. $C_{31}H_{40}O_{12}N_2$ requires C, 58·9; H, 6·3; N, 4·4%). The action of nitric acid on it produced the same nitroso-acid as was obtained by the oxidation of aconitine with nitric acid.

The micro-analyses were carried out by Roth, Heidelberg, and Schoeller, Berlin.

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18. *The Interaction of Diazonium Salts and Acetonesulphonic Acid.*

By G. D. PARKES and S. J. M. FISHER.

ACETONESULPHONIC acid, like ω-nitroacetophenone (Parkes and Williams, J., 1934, 67) and acetophenone-ω-sulphonic acid (Parkes and Tinsley, *ibid.*, p. 1861), contains a reactive methylene group and couples readily with diazonium salts in presence of sodium acetate to produce *methylglyoxalarylhydrazone-ω-sulphonates*:

$$R{\cdot}N_2Cl + CH_3{\cdot}CO{\cdot}CH_2{\cdot}SO_3Na \longrightarrow R{\cdot}NH{\cdot}N{:}C(SO_3Na){\cdot}CO{\cdot}CH_3$$

The yields are not so good as those from acetophenone-ω-sulphonic acid owing to the formation of dark red by-products.

The action of bromine upon sodium methylglyoxalphenylhydrazonesulphonate is in the main similar to its action upon the corresponding acetophenone derivative (Parkes and Tinsley, *loc. cit.*); with one molecular proportion of bromine, however, the reaction cannot be interrupted at the *p*-bromophenylhydrazone stage, and the product is a mixture of unchanged material and ω-bromomethylglyoxal-*p*-bromophenylhydrazone, the sulpho-group having been replaced by bromine. With two molecules of bromine, an almost theoretical yield of ω-bromomethylglyoxal-*p*-bromophenylhydrazone is obtained. This

compound also results from the action of one molecule of bromine upon methylglyoxal-*p*-bromophenylhydrazone-ω-sulphonic acid. The further action of bromine results in the formation of βω-dibromo-α-ketopropaldehyde-*p*-bromophenylhydrazone (compare Chattaway aud Ashworth, J., 1934, 930).

$$C_6H_5{\cdot}NH{\cdot}N{:}C(SO_3Na){\cdot}COMe \longrightarrow [C_6H_4Br{\cdot}NH{\cdot}N{:}C(SO_3Na){\cdot}COMe] \longrightarrow C_6H_4Br{\cdot}NH{\cdot}N{:}CBr{\cdot}COMe \longrightarrow C_6H_4Br{\cdot}NH{\cdot}N{:}CBr{\cdot}CO{\cdot}CH_2Br$$

The action of excess of bromine on sodium methylglyoxal-2 : 4-dibromophenylhydrazone-ω-sulphonate similarly yields ββω-tribromo-α-ketopropaldehyde-2 : 4-dibromophenylhydrazone :

$$C_6H_4Br_2{\cdot}NH{\cdot}N{:}C(SO_3Na){\cdot}COMe \longrightarrow C_6H_4Br_2{\cdot}NH{\cdot}N{:}CBr{\cdot}CO{\cdot}CHBr_2$$

Experimental.

Sodium Acetonesulphonate.—Monobromoacetone (Levene, "Organic Syntheses," 1930, **10**, 12) (180 g.), dissolved in 75 c.c. of alcohol, was added to 375 g. of crystallised sodium sulphite in 375 c.c. of water, the solution evaporated to dryness on the water-bath, and the residue extracted several times with boiling alcohol. Sodium acetonesulphonate separated from the extract on cooling; it was dried, and preserved over calcium chloride in a vacuum desiccator (compare Bender, *Z. Chem.*, 1870, 162).

*Sodium Methylglyoxal-*p*-bromophenylhydrazone-ω-sulphonate.*—A solution of 21 g. of *p*-bromoaniline in 5 c.c. of hot glacial acetic acid was poured into a mixture of 25 c.c. of concentrated hydrochloric acid and 25 c.c. of water with vigorous stirring. This was diazotised with 9 g. of sodium nitrite and added with stirring during ½ hour to a mixture of 20 g. of sodium acetonesulphonate, 200 g. of crystallised sodium acetate, and 200 c.c. of water at 0°. The liquid was filtered after 20 hours and the *sodium methylglyoxal-*p*-bromophenylhydrazone-ω-sulphonate* (coloured deep red by a by-product) was washed with a little warm water to remove sodium acetate, extracted with several very small quantities of hot alcohol to remove the red impurity, and crystallised from boiling alcohol (charcoal), from which it separated in fine, pale yellow needles, m. p. 224° (decomp.) (Found : N, 8·0. $C_9H_8O_4BrSNa$ requires N, 8·2%).

The following sodium salts were obtained similarly: *methylglyoxalphenylhydrazone-ω-sulphonate*, pale yellow needles, m. p. 195° (decomp.) (Found : N, 10·4. $C_9H_9O_4N_2SNa$ requires N, 10·6%); *methylglyoxal-*p*-chlorophenylhydrazone-ω-sulphonate*, lemon-yellow needles, m. p. 228° (decomp.) (Found : Cl, 11·75. $C_9H_8O_4N_2ClSNa$ reqnires Cl, 11·9%); *methylglyoxal-2 : 4-dichlorophenylhydrazone-ω-sulphonate*, yellow needles from methyl alcohol, m. p. 270° (decomp.) (Found : N, 8·25. $C_9H_7O_4N_2Cl_2SNa$ requires N, 8·4%); *methylglyoxal-2 : 4-dibromophenylhydrazone-ω-sulphonate*, yellow needles from methyl alcohol, m. p. 275° (decomp.) (Found : N, 6·6. $C_9H_7O_4N_2Br_2SNa$ requires N, 6·6%); *methylglyoxal-*o*-nitrophenylhydrazone-ω-sulphonate*, deep golden, microcrystalline powder, m. p. 256° (decomp.) (Found : N, 13·5. $C_9H_8O_6N_3SNa$ requires N, 13·6%); *methylglyoxal-*m*-nitrophenylhydrazone-ω-sulphonate*, pale yellow plates from glacial acetic acid, m. p. 251° (decomp.) (Found : N, 13·2%); *methylglyoxal-*p*-nitrophenylhydrazone-ω-sulphonate*, yellow prismatic needles from methyl alcohol, m. p. 265° (decomp.) (Found : N, 13·4%).

Action of Bromine upon Sodium Methylglyoxalphenylhydrazone-ω-sulphonate.—(1) 1 *Mol. of bromine.* 1·6 G. of bromine (1 mol.) in a few c.c. of glacial acetic acid were added with shaking to 2·6 g. of sodium methylglyoxalphenylhydrazone-ω-sulphonate in 40 c.c. of glacial acetic acid. The deep red liquid was filtered from unchanged initial material, heated to 100°, and diluted with hot water until it was just turbid; on cooling, ω-bromomethylglyoxal-*p*-bromophenylhydrazone separated, identical with a specimen prepared by Chattaway and Lye's method (*Proc. Roy. Soc.*, 1932, *A*, **137**, 489).

(2) 2 *Mols. of bromine.* When 3·2 g. of bromine were used, the other quantities being as in (1), a clear solution was obtained, from which ω-bromomethylglyoxal-*p*-bromophenylhydrazone was precipitated by dilution with hot water.

(3) 3 *Mols. of bromine.* 2·6 G. of sodium methylglyoxalphenylhydrazone-ω-sulphonate in 20 c.c. of glacial acetic acid were treated with 4·8 g. of bromine in 5 c.c. of glacial acetic acid. By diluting the hot solution with hot water as above, βω-dibromo-α-ketopropaldehyde-*p*-bromophenylhydrazone was obtained; this crystallised from alcohol in bright yellow, hair-like needles, m. p. 174—175°, identical with a specimen prepared by Chattaway and Ashworth's method (*loc. cit.*).

(4) *Excess of bromine.* The action of excess of bromine upon sodium methylglyoxal-2 : 4-dibromophenylhydrazone-ω-sulphonate dissolved in glacial acetic acid was carried out in a similar manner. The product was ββω-*tribromo*-α-*ketopropaldehyde*-2 : 4-*dibromophenylhydrazone*, identical with a specimen prepared by Chattaway and Lye's method (*loc. cit.*).

The Dyson Perrins Laboratory, Oxford University. [*Received, November 6th,* 1935.]

19. *The (+) and (−) γ-Phenyl-α-methylallyl Alcohols.*

By J. Kenyon, S. M. Partridge, and H. Phillips.

Recrystallisation of the cinchonidine salt of *dl*-γ-phenyl-α-methylallyl hydrogen phthalate yields the optically pure (+) hydrogen phthalic ester: the (−) hydrogen phthalic ester can be obtained by recrystallisation of the corresponding brucine salt. The rotatory powers (± 44·6°) of the two hydrogen phthalic esters thus obtained are unchanged when the esters are recrystallised, although *d* + *dl*-hydrogen phthalic esters obtained from incompletely resolved alkaloidal salts can be separated by crystallisation from solvents, notably carbon disulphide, into pure *dl*- and *d*-(+)-hydrogen esters. The specific rotatory powers of the (+) hydrogen ester in various solvents are in Table I. When saponified with sodium carbonate solution, these esters give unexpectedly the *dl*-alcohol. The optically active alcohols can be obtained, however, by saponifying the hydrogen phthalic esters with sodium hydroxide solution: the more concentrated the solution employed, the higher the rotatory powers of the resulting alcohols. Even under the most favourable experimental conditions some racemisation occurs, since the rotatory power and the melting point of the optically active alcohols obtained can be raised by recrystallisation, being finally m. p. 61° and $[\alpha]_{5461}$ + 28·3° (in carbon disulphide) for the alcohol obtained from a mixture of methylene chloride and light petroleum. The recrystallised alcohol when reconverted into its hydrogen phthalic ester gives a product of rotatory power identical with that of the hydrogen phthalic ester from which it has been obtained.

A high concentration of hydroxyl ions thus appears to favour the reaction which leads to the carbinol of the same configuration as the reacting hydrogen phthalic ester, as is the case when the hydrogen phthalic esters of saturated alcohols undergo saponification. At lower concentrations of hydroxyl ions, part of the hydrogen phthalic ester presumably reacts with intermediate formation of a carbonium cation, leading to inversion and racemisation—a type of scission which is possible in esters of substituted allyl alcohols (cf. Burton and Ingold, J., 1928, 904).

Table I.

Specific Rotatory Powers of (+) γ-Phenyl-α-methylallyl Hydrogen Phthalate in Various Solvents at Room Temperature (1, 2; c, 5·00).

Solvent.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	Solvent.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
CS_2	+37·38°	+39·00°	+44·71°	+87·4°	$COMe_2$ ...	−10·3°	−11·8°	−12·6°	−22·3°
C_5H_5N	+19·8	+21·2	+24·2	+43·0	Et_2O	−13·9	−14·5	−18·3	−32·2
$C_2H_4O_2$	+19·1	—	+23·8	+47·6	$C_2H_4Br_2$ ...	− 8·9	—	−11·1	−19·6
C_6H_6	+ 4·0	+ 4·7	+ 5·1	+ 7·8	$CH_3{\cdot}CO_2Et$	−10·0	—	−23·7	−41·5
CCl_4	+ 3·3	+ 4·7	+ 4·9	+ 7·2	Dioxan ...	− 7·2	− 8·2	− 9·2	−17·7
$CHCl_3$	+ 1·8	+ 2·0	+ 2·2	+ 5·3	(−) γ-Phenyl-α-methylallyl Hydrogen Phthalate.				
MeOH (*c*, 14·6)	− 7·2	− 7·4	− 8·4	−15·3					
EtOH	−13·5	−14·1	−15·4	−28·0	CS_2.........	−36·23	−37·39	−44·53	−88·74

The (+) alcohol thus obtained can be reduced to (−) methyl-β-phenylethylcarbinol having a rotatory power in close agreement with that of the *l*-methyl-β-phenylethylcarbinol obtained by direct resolution (Pickard and Kenyon, J., 1914, **105**, 1124). This affords fairly conclusive evidence that (+) and (−) γ-phenyl-α-methylallyl alcohol have been isolated in an optically pure state. In Table II, the rotatory powers of the (+) alcohol are compared with those of (−) methyl-β-phenylethylcarbinol.

The rotatory powers of (+) butan-2-ol and (+) methylvinylcarbinol are also included in this table because they show (a) that, when the hydrogen atom in the β-position (with

TABLE II.

	$[\alpha]_{5461}^{20°}$.	$\alpha_{4358}/\alpha_{5461}$.	$[M]_{5461}^{20°}$.
(−) $CH_2Ph{\cdot}CH_2{\cdot}CHMe{\cdot}OH$	− 16·75°	1·870	− 25·12°
(−) $CH_3{\cdot}CH_2{\cdot}CHMe{\cdot}OH$	− 16·10	1·662	− 11·91
(+) $CHPh{:}CH{\cdot}CHMe{\cdot}OH$	+ 39·48	2·06	+ 58·43
(+) $CH_2{:}CH{\cdot}CHMe{\cdot}OH$ *	+ 40·38	1·802	+ 29·07

* Kenyon and Snellgrove, J., 1925, **127**, 1169.

respect to the hydroxyl group) in both the saturated and the unsaturated aliphatic alcohol is replaced by a phenyl group, the molecular rotatory powers are approximately doubled, (b) that the introduction of a Δ^{α}-bond into both the aliphatic and the semi-aromatic alcohol not only more than doubles the rotatory power but also reverses its sign. In compiling this table it has been assumed that (−) methylvinylcarbinol has the same configuration as (+) butan-2-ol, since (−) *n*-butylvinylcarbinol has been proved to have the same configuration as (+) ethyl-*n*-butylcarbinol (Levene and Haller, *J. Biol. Chem.*, 1929, **83**, 579; Johnson and Kenyon, J., 1932, 722).

In Table III, the properties of (+) γ-phenyl-α-methylallyl alcohol and its derivatives are compared with those of the corresponding saturated alcohol, (+) methyl-β-phenylethylcarbinol.

TABLE III.

	(+) Methyl-β-phenylethylcarbinol.	(+) γ-Phenyl-α-methylallyl alcohol.
(+) Alcohol		
$\alpha_{5461}^{50°}$	+ 16·94° *	+ 42·0°
$\alpha_{4358}^{50°}/\alpha_{5461}^{50°}$	1·680	2·06
Acetate of (+) alcohol		
$\alpha_{5461}^{20°}$	1·72° †	− 166·0°
$\alpha_{4358}^{20°}/\alpha_{5461}^{20°}$	0·2	1·928
Hydrogen phthalate of (+) alcohol		
$[\alpha]_{5893}$ (*c*, 5 in ethyl alcohol)	+ 54·4°	− 15·4°
M. p.	oil	92—93·5°
Hydrogen phthalate of *dl*-alcohol		
M. p.	oil	68·5°

* Pickard and Kenyon, *loc. cit.* † Hewitt and Kenyon, J., 1925, **127**, 1094.

TABLE IV.

Variation of Rotatory Power of (+) γ-Phenyl-α-methylallyl Alcohol with Temperature (l, 0·5).

t.	α_{5780}.	α_{5461}.	α_{4358}.	*t*.	α_{5780}.	α_{5461}.	α_{4358}.
51°	+ 17·96°	+ 21·00°	+ 43·23°	74·5°	+ 16·54	+ 19·26°	+ 39·65°
59·5	17·66	20·68	41·56	95·0	15·28	17·82	35·63

TABLE V.

Specific Rotatory Powers of (+) γ-Phenyl-α-methylallyl Alcohol in Various Solvents (l, 2·0) *at Room Temperature.*

Solvent.	G. per 100 c.c. soln.	α_{5893}.	α_{5780}.	α_{5461}.	α_{4358}.
C_5H_5N	5·000	+28·8°	+32·3°	+36·5°	+73·3°
$CHCl_3$	5·000	24·7	26·5	30·9	60·7
CS_2	5·000	23·65	25·0	28·3	59·3
Et_2O	5·000	22·2	24·8	28·5	54·5
EtOH	5·000	18·5	20·8	23·7	49·0

Solvent.	G. per 100 c.c. soln.	α_{5893}.	α_{5780}.	α_{5461}.	α_{4358}.
C_6H_6	4·070	+18·2°	+19·4°	+22·2°	+43·0°
$COMe_2$	5·000	16·8	19·1	21·8	45·0
(−) γ-Phenyl-α-methylallyl Alcohol.					
CS_2	4·498	−23·55	−24·1	−28·0	−56·0

EXPERIMENTAL.

dl-γ-Phenyl-α-methylallyl alcohol (119 g.), prepared by the addition of cinnamaldehyde (126 g.) to the Grignard reagent obtained from magnesium (24 g.) and methyl bromide (98 g.), had b. p. 129—131°/11 mm. It set to a mass of small, irregular, prismatic needles, m. p. 30—31·5°. Its phenylurethane separated from ether and petroleum in fine hairy needles, m. p. 93—94° (Klages, *Ber.*, 1902, **35**, 2650, gives m. p. 94—95°), and its p-*xenylurethane* from benzene in rosettes of small needles, m. p. 162—163° (Found: N, 4·3. $C_{23}H_{21}O_2N$ requires N, 4·1%).

Attempts were made to separate *dl*-γ-phenyl-α-methylallyl alcohol into *cis*- and *trans*-forms by (a) fractional distillation, (b) partial fusion of the solidified alcohol and draining of the liquefied portion, and (c) crystallisation from methylene chloride and light petroleum. The various fractions of the alcohol from (a) and (b) all had m. p. 30—31·5°; the alcohol after crystallisation from methylene chloride and light petroleum, from which it separated in spherical clusters of fine needles, had m. p. 33°.

dl-*γ-Phenyl-α-methylallyl* p-*nitrobenzoate* was prepared from *p*-nitrobenzoyl chloride (18·8 g.), *dl*-γ-phenyl-α-methylallyl alcohol (14·8 g.), and pyridine (10 g.). The solid product was taken up in ether and sodium carbonate solution. The dried ethereal solution was evaporated to small bulk and mixed with light petroleum; the *p*-nitrobenzoate (22 g., m. p. 56—58°) on recrystallisation formed almost colourless, short, fine needles, m. p. 58—59° (Found: N, 4·7. $C_{17}H_{15}O_4N$ requires N, 4·7%).

dl-*γ-Phenyl-α-methylallyl Hydrogen Phthalate*.—(i) A mixture of the alcohol (148 g.), phthalic anhydride (148 g.), and pyridine (100 g.), heated for 1½ hours on the steam-bath, became a homogeneous viscous liquid. Next day the product was dissolved in acetone (500 c.c.) and mixed with ice-cold dilute hydrochloric acid; the liberated oil, when stirred with a large volume of water, soon set to a crystalline mass (218 g., m. p. 85—90°). The hydrogen phthalic ester separated from carbon disulphide or from ether–light petroleum in irregular glassy rhombs, m. p. 92—93·5°.

(ii) Phthalic anhydride (3·5 g.) was added to the Grignard complex obtained by the interaction in ethereal solution of magnesium (0·3 g.), methyl iodide (3·6 g.), and subsequently of cinnamaldehyde (3·2 g.) and the resultant paste was triturated for a few minutes until it changed into a yellowish-brown powder easily removable by filtration. This was taken up in ether and dilute sodium carbonate solution: the sodium carbonate extracts on addition of hydrochloric acid gave an oil which rapidly crystallised. The hydrogen phthalic ester (2·5 g., m. p. 90—91°) separated from carbon disulphide in glassy rhombs, m. p. and mixed m. p. 92—93° (Found by titration with sodium hydroxide: *M*, 293. $C_{18}H_{16}O_4$ requires *M*, 296). Repeated crystallisation of *dl*-γ-phenyl-α-methylallyl hydrogen phthalate did not alter its m. p. and the *dl*-γ-phenyl-α-methylallyl alcohol obtained from it by saponification had b. p. 129°/10 mm., m. p. 30—31·5°, $d_{4°}^{17·2°}$ 1·072, $d_{4°}^{27·4°}$ 1·040, $d_{4°}^{36·5°}$ 1·012, $d_{4°}^{43·2°}$ 0·990, $n_D^{10°}$ 1·5741, $n_D^{20°}$ 1·5692, $n_D^{62°}$ 1·5521, [*P*] 367·4 (mean value between 17° and 43°) (calc., 372·1).

(+) *γ-Phenyl-α-methylallyl Hydrogen Phthalate*.—Cinchonidine (30 g.) was dissolved in a hot solution of the *dl*-hydrogen phthalic ester (30 g.) in ethyl acetate (90 c.c.). The cinchonidine salt of (+) γ-phenyl-α-methylallyl hydrogen phthalate (25 g.) separated on cooling: it was obtained optically pure in tufts of fibrous needles (7·5 g.), m. p. 179° (decomp.), with $[\alpha]_{5893}$ − 28·9°, $[\alpha]_{5780}$ − 30·1°, $[\alpha]_{5461}$ − 36·4°, $[\alpha]_{4358}$ − 59·2° (*c*, 5·050; *l*, 2) in chloroform solution. On decomposition with dilute hydrochloric acid it yielded (+) γ-phenyl-α-methylallyl hydrogen phthalate, which crystallised from carbon disulphide and light petroleum in felted masses of fine hairy needles, m. p. 68·5° (unchanged after 18 months). The rotatory powers are in Table I.

(+) *γ-Phenyl-α-methylallyl Alcohol*.—The alcohol of highest rotatory power was obtained when the following procedures were followed: (a) the (+) hydrogen phthalic ester (30 g.) was heated for 1 hour on the steam-bath with 5*N*-sodium hydroxide (45 c.c.), and the mixture distilled in steam. Extraction of the distillate yielded the (+) alcohol (13 g.), b. p. 128°/10 mm., m. p. 49—50°, $\alpha_{5893}^{20°}$ + 6·4°, $\alpha_{5461}^{20°}$ + 7·5°, $\alpha_{4358}^{20°}$ + 14·4° (*l*, 0·25). After being kept in a closed vessel for nearly two years, the alcohol had $\alpha_{5893}^{26°}$ + 11·86° (*l*, 0·5).

(b) The (−) hydrogen phthalic ester (12 g.) in hot ethyl alcohol (40 c.c.) was mixed with 5*N*-sodium hydroxide (30 c.c.) and heated under reflux for 15 minutes. Distillation in steam removed the alcohol, which solidified in the distillate. After drying, it had m. p. 55° and $[\alpha]_{5461}$ − 21·2° in carbon disulphide solution (*c*, 5·00; *l*, 2).

Even under these conditions some racemisation occurred, since both the rotatory power and the m. p. of the alcohol were raised by crystallisation. That from experiment (b) after one crystallisation from methylene chloride–light petroleum had m. p. 61°, $n_D^{28°}$ 1·5486, and $[\alpha]_{5461}$ − 28·0° (*c*, 5·00; *l*, 2) in carbon disulphide solution. The maximum values obtained are in Tables IV and V.

(−) *γ-Phenyl-α-methylallyl Hydrogen Phthalate*.—The first filtrate from the crystallisation of the cinchonidine salt yielded a hydrogen phthalic ester (18 g.) with $[\alpha]_{5461}$ − 24° (*c*, 5 in carbon disulphide). In a solution of this in acetone (30 c.c.), brucine (24 g.) was dissolved. On cooling, the brucine salt of (−) γ-phenyl-α-methylallyl hydrogen phthalate separated in small needles; it was obtained optically pure after two further crystallisations from acetone; decomp. about 110°, $[\alpha]_{5893}$ − 31·0°, $[\alpha]_{5780}$ − 36·9°, $[\alpha]_{5461}$ − 48·7°, $[\alpha]_{4358}$ − 102·0° (*c*, 5·325; *l*, 2) in chloroform

solution. On decomposition of the brucine salt with hydrochloric acid (−) γ-phenyl-α-methylallyl hydrogen phthalate was obtained. It separated from carbon disulphide and light petroleum in masses of felted needles, m. p. 68·5°.

The optically active forms of γ-phenyl-α-methylallyl hydrogen phthalate are much more soluble than the inactive variety: when carbon disulphide solutions containing equal amounts of the *d*- and the *l*-form were mixed, the crystals which separated were glassy rhombs of the *dl*-hydrogen phthalic ester, m. p. 92—93°.

(−) γ-Phenyl-α-methylallyl alcohol, obtained from the (−) hydrogen phthalic ester, crystallised from methylene chloride and light petroleum in large hexagonal plates or long four-sided prisms, m. p. 61°. Equal amounts of (+) and (−) γ-phenyl-α-methylallyl alcohol of m. p. 61° were fused together; after solidification the *dl*-product had m. p. 33·5°.

(+) γ-Phenyl-α-methylallyl alcohol, $[\alpha]_{5461}$ + 28·3° (*c*, 5·0; *l*, 2 in carbon disulphide solution), was reconverted into its hydrogen phthalic ester; this had m. p. 68° and $[\alpha]_{5461}$ + 44·7° (*c*, 2·905; *l*, 2) in carbon disulphide solution.

The p-*xenylurethane* of (+) *γ-phenyl-α-methylallyl alcohol* formed needles, m. p. 179—180°, from methylene chloride and light petroleum; it had $[\alpha]_{5893}$ + 163·3°, $[\alpha]_{5780}$ + 176·6°, $[\alpha]_{5461}$ + 200·1°, $[\alpha]_{4358}$ + 408° (*c*, 0·6385; *l*, 2) in chloroform solution (Found: N, 4·2. $C_{23}H_{21}O_2N$ requires N, 4·1%).

(+) γ-Phenyl-α-methylallyl acetate, prepared by gently heating a mixture of the (+) alcohol (5 g.), pyridine (4 g.), and acetic anhydride (5 g.), had b. p. 132—133°/9 mm., $n_D^{12°}$ 1·5369, $\alpha_{5893}^{20°}$ + 34·16°, $\alpha_{5780}^{20°}$ + 35·78°, $\alpha_{5461}^{20°}$ +41·51°, $\alpha_{4358}^{20°}$ + 80·0° (*l*, 0·25); in chloroform solntion (*c*, 5·020; *l*, 2) it had $[\alpha]_{5893}$ + 132·8°, $[\alpha]_{5750}$ + 86·2°, $[\alpha]_{5461}$ + 108·7°, $[\alpha]_{4358}$ + 308·3°.

(+) *γ-Phenyl-α-methylallyl* p-*nitrobenzoate* formed leaflets, m. p. 41°, from ether–light petroleum (Found: N, 4·8. $C_{17}H_{15}O_4N$ requires N, 4·7%); it had $[\alpha]_{5893}$ − 27·0°, $[\alpha]_{5780}$ − 27·5°, $[\alpha]_{5461}$ − 33·5°, $[\alpha]_{4358}$ − 87·4° (*c*, 4·450; *l*, 2) in chloroform solution.

Reduction of (+) *γ-Phenyl-α-methylallyl Alcohol to* (−) *Methyl-β-phenylethylcarbinol.*—The alcohol (4·4 g. with $[\alpha]_{5893}$ + 23·65° in carbon disulphide solution) was reduced with hydrogen in the presence of a platinum catalyst prepared by the method of Adams, Voorhees, and Skriner ("Organic Syntheses," **8**, 92). The calculated volume of hydrogen was absorbed within 1 hour. The resulting (−) methyl-β-phenylethylcarbinol, which had no action on bromine solution, had b. p. 127°/16 mm., and $\alpha_{5893}^{18°}$ − 3·42°, $\alpha_{5780}^{18°}$ − 3·59°, $\alpha_{5461}^{18°}$ − 4·04°, $\alpha_{4358}^{18°}$ − 6·69° (*l*, 0·25). Its *phenylurethane* (Found: N, 5·4. $C_{17}H_{19}O_2N$ requires N, 5·2%) had m. p. 47—48° alone or mixed with a specimen prepared from the alcohol of Pickard and Kenyon. The rotatory powers given by Pickard and Kenyon (*loc. cit.*) for this alcohol prepared by direct resolution are $\alpha_{5461}^{18.5°}$ − 4·10°, $\alpha_{4358}^{18.5°}$ − 6·85° (*l*, 0·25). The specimen prepared by Pickard and Kenyon was found after some 22 years to have (without redistillation) the following rotatory powers: $\alpha_{5461}^{19°}$ − 3·88°, $\alpha_{4358}^{19°}$ − 6·52° (*l*, 0·25).

In view of the change in the sign of rotatory power undergone by (+) γ-phenyl-α-methylallyl alcohol after its conversion into (−) methyl-β-phenylethylcarbinol it is interesting to note that, whereas the less soluble cinchonidine salt of the hydrogen phthalic ester of the former gives rise to the (+) alcohol and the less soluble brucine salt of the hydrogen phthalic ester to the (−) alcohol, the converse is the case with the latter, the less soluble cinchonidine salt of the hydrogen phthalic ester yielding the (−) alcohol and the corresponding brucine salt the (+) alcohol.

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BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, November 7th*, 1935.]

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20. *Chemotherapeutic Studies in the Acridine Series. Part I. 2 : 6- and 2 : 8-Diaminoacridines.*

By ADRIEN ALBERT and WILFRED H. LINNELL.

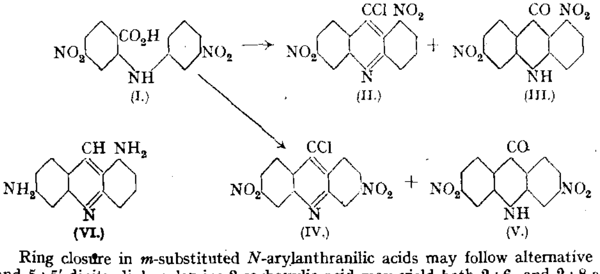
THE use of acridine derivatives as bactericides was first suggested by Browning and co-workers (*Brit. Med. J.*, 1917, 73), who introduced proflavine (2 : 8-diaminoacridine sulphate) and the corresponding methochloride (acriflavine). In 1922, Browning, Cohen, Gaunt, and Gulbransen (*Proc. Roy. Soc.*, 1922, *B*, **93**, 329) showed by synthesis that the bactericidal

properties of proflavine were due to the acridine molecule as a whole, and were not shown by corresponding derivatives of pyridine, quinoline, hydroquinoline or naphthaquinoline. In addition, they tried the effects of various substituents in the molecule of 2 : 8-diamino-acridine, but the products rarely equalled and in no case excelled the parent compound in activity. In 1930, Bogert and co-workers (*Coll. Czech. Chem. Comm.*, 1930, **2**, 383) made and tested 3 : 7-diaminoacridine. Beyond this, no attempt has been made to investigate the chemotherapeutic effects of placing the amino-groups elsewhere in the ring.

It was therefore decided to attempt the preparation and to investigate the bactericidal properties of the twenty possible diaminoacridines, of which seventeen are unknown. This work will provide an opportunity for studying ring closure in the series.

The 2 : 6-*Diaminoacridine Series.*—5 : 5′-*Dinitrodiphenylamine-2-carboxylic acid* (I) was obtained in 28% yield, together with 30% of *p*-nitrobenzoic acid, by condensing sodium 2-chloro-4-nitrobenzoate with *m*-nitroaniline in presence of copper. When *cyclo*hexanol replaced the 4-methyl*cyclo*hexanol used as solvent, another by-product, 5 : 5′-dinitro-diphenic acid (m. p. 289°; anhydride, m. p. 266°), was obtained in quantities up to 18%. Tuttle (*J. Amer. Chem. Soc.*, 1923, **45**, 1906) obtained 4 : 4′-dinitrodiphenic acid from the condensation of 2-chloro-5-nitrobenzoic acid with diethyl-*m*-phenylenediamine. The constitution of the 5 : 5′-dinitrodiphenylamine-2-carboxylic acid was confirmed by an alternative synthesis from *m*-bromonitrobenzene and 4-nitroanthranilic acid.

Although several nitrodiphenylamine-2-carboxylic acids have been reduced to the corresponding amino-acids (Graebe, *Annalen*, 1893, **276**, 41; Ullmann, *ibid.*, 1907, **355**, 351), reduction of the above dinitrodiphenylaminecarboxylic acid gave 3 : 3′-*diamino-diphenylamine*. The loss of carbon dioxide in this reaction is not an isolated instance (cf. Seidel *et al.*, *Monatsh.*, 1902, **23**, 434): Blanksma (*Rec. trav. chim.*, 1905, **24**, 320) suggested, for simple benzoic acids, that the deciding factor is a nitro-group meta to the amino-group and para to the carboxyl. The above example, and others shortly to be published, suggest that this contention applies also to the *N*-alkylanthranilic acids. 3 : 3′-Diaminodiphenylamine was characterised by its *diacetyl* derivative and by its identity with the product of reduction of 3 : 3′-*dinitrodiphenylamine* obtained by the condensation of *m*-nitroaniline with *m*-bromonitrobenzene. This dinitrodiphenylamine was obtained in better yield by a method similar to that used for analogous substances by Goldberg (*Ber.*, 1907, **40**, 4541), notwithstanding that Ryan and Glover (*Proc. Roy. Irish Acad.*, 1918, **34**, *B*, 97) failed to make it by the Goldberg reaction.



Ring closure in *m*-substituted *N*-arylanthranilic acids may follow alternative routes, and 5 : 5′-dinitrodiphenylamine-2-carboxylic acid may yield both 2 : 6- and 2 : 8-acridine derivatives. Closure by means of excess of phosphorus oxychloride (cf. Lesnianski, *Bull. Acad. Polonaise*, 1929, 81) favours the formation of the 2 : 6-compound, for a quantitative yield of a mixture of acridine compounds was obtained, of which the principal member was the required 5-*chloro*-2 : 6-*dinitroacridine* (II), accompanied by 2 : 6-*dinitroacridone* (III) and smaller amounts of the corresponding 2 : 8-compounds (IV and V), which formed approximately 10% of the products. When less phosphorus oxychloride was used and

the product was treated with warm water (cf. Magidson, *Ber.*, **1933**, **66**, 866), a quantitative yield was obtained of 2 : 6- and 2 : 8-dinitroacridones free from chlorinated products, but no advantage was to be gained by following this route owing to the difficulty of separating these isomerides. The chlorodinitroacridines were separated by fractional crystallisation. 5-Chloro-2 : 6-dinitroacridine, unlike the 5-chloroacridine of Graebe (*Annalen*, 1893, **276**, 48), does not evolve a vapour attacking the mucous membranes, but in the solid condition it causes considerable irritation when allowed to remain in contact with the skin. Its constitution is confirmed by the series of compounds formed in the subsequent reactions, a series closely mirrored by those formed by similar transformation of the isomeric 2 : 8-compound, which led to well-known end-products.

On hydrolysis of (II) with dilute acid, 2 : 6-dinitroacridone was quantitatively formed. Reduction of this with stannous chloride gave a good yield of 2 : 6-*diaminoacridone* as its stannichloride. The base and the 2 : 8-isomeride (*v.i.*) differ markedly in physical properties but are very similar in chemical properties.

On reduction with sodium amalgam, 2 : 6-diaminoacridone gave 2 : 6-*diaminoacridine* (VI). This differed from its 2 : 8-isomeride by not exhibiting fluorescence in any solvent, but closely resembled it in chemical properties. Its bactericidal properties are under investigation.

The 2 : 8-Diaminoacridine Series.—5-Chloro-2 : 8-dinitroacridine (IV) resembled the 2 : 6-isomeride in physical and chemical properties very closely, but differed in not exhibiting fluorescence in ultra-violet light. Hydrolysis with dilute acids gave 2 : 8-dinitroacridone (V). The constitutions of these two substances follow from analogy with the corresponding 2 : 6-isomerides, and from the reduction of 2 : 8-dinitroacridone with stannous chloride to 2 : 8-diaminoacridone (Schöpff, *Ber.*, 1894, **27**, 2316). Further reduction with sodium amalgam and aqueous sodium hydroxide gave 2 : 8-diaminoacridine in 90% yield.

EXPERIMENTAL.

5 : 5'-Dinitrodiphenylamine-2-carboxylic Acid (I).—Condensation of 2-chloro-4-nitrobenzoic acid with *m*-nitroaniline by the usual methods (Jourdan, *Ber.*, 1885, **18**, 1448; Cohn, *Monatsh.*, 1901, **22**, 385; Ullmann, *Annalen*, 1907, 355, 330; Perkin *et al.*, J., 1924, **125**, 1784) either failed or gave insignificant yields. Sodium 2-chloro-4-nitrobenzoate (4·5 g.), *m*-nitroaniline (5·6 g.; 2 mols.), freshly precipitated copper (0·1 g.), and 4-methyl*cyclo*hexanol (20 ml.) were refluxed together for 1 hour; sodium carbonate (2 g.) was added and after steam-distillation the liquid was filtered. The sodium salt that separated from the filtrate yielded on acidification 5 : 5'-*dinitrodiphenylamine-2-carboxylic acid* (I), which crystallised from alcohol in brownish-orange crystals, m. p. 263° (corr.), almost insoluble in petroleum spirit, dilute mineral acids, and hot and cold water, sparingly soluble in benzene, toluene, and chloroform, and soluble in boiling glacial acetic acid (approx. 1 in 20) and 97% alcohol (approx. 1 in 29, boiling; 1 in 120, cold) (Found: C, 51·7; H, 3·0; N, 14·2. $C_{13}H_9O_6N_3$ requires C, 51·5; H, 3·0; N, 13·9%). Increasing the quantities of material treated at a time decreased the yield considerably, as did also the use of other varieties of solvent or copper. The almost colourless solution of the acid in sulphuric acid becomes yellow on addition of a trace of a nitrate. The alkali salts are freely soluble in hot, and sparingly in cold, water, and are readily salted out. The sodium salt consists of reddish-orange longitudinal plates. The *silver* salt is bright yellow, soluble in aqueous ammonia, and insoluble in boiling water (Found: Ag, 26·0. $C_{13}H_8O_6N_3Ag$ requires Ag, 26·3%). The calcium salt forms orange-brown crystals, soluble in hot, insoluble in cold water. The above acid, m. p. and mixed m. p. 263°, was similarly obtained in 4% yield by refluxing *m*-bromonitrobenzene, 4-nitro-2-aminobenzoic acid, sodium carbonate, and precipitated copper in 4-methyl*cyclo*hexanol for 16 hours and fractionally crystallising the calcium salts of the acids remaining after steam-distillation.

Reduction of the above acid with sodium sulphide, yellow ammonium sulphide, sodium hyposulphite, or stannous chloride gave no trace of amino-acid.

3 : 3'-Diaminodiphenylamine.—5 : 5'-Dinitrodiphenylamine-2-carboxylic acid (6 g.) was added to a hot solution of stannous chloride (35 g.) in 10% hydrochloric acid (100 ml.). The solution was concentrated and cooled and the stannichloride was collected, washed with ether, and dissolved in hot water. After removal of tin with hydrogen sulphide the filtrate was saturated with sodium acetate and the precipitated *amine* (yield, 68%) was repeatedly crystallised

from boiling water (1 in 105), forming white needles, m. p. 94·5—95°, soluble in cold alcohol, hot benzene, and toluene, but precipitated from the latter with petroleum spirit (Found: C, 71·9; H, 6·7; N, 21·2. $C_{12}H_{13}N_3$ requires C, 72·4; H, 6·6; N, 21·1%). The base decomposes on even gentle warming, becoming pink on exposure to the air; it is diazotisable and then couples with β-naphthol (scarlet). The salts with mineral acids are freely soluble. The solution in concentrated sulphuric acid becomes intense brown with a trace of a nitrate, and bright pink with a trace of ferrous sulphate and a drop of hydrogen peroxide solution. The aniline sulphate–dichromate test gives a brown precipitate, an ethereal extract of which is purple and becomes green when well acidified. The 3 : 3′-*bisacetyl* derivative, formed by the action of acetic anhydride in ether (yield, 95%), formed minute white crystals, m. p. 211° (corr.) (from 35% alcohol), insoluble in hot water, soluble in boiling alcohol (approx. 1 in 15 of 97%) and boiling glacial acetic acid, but the recovery on cooling from both of these was poor (Found: N, 14·4. $C_{16}H_{17}O_2N_3$ requires N, 14·9%). The amine is readily regenerated by boiling hydrochloric acid; both substances fluoresce brightly in ultra-violet light, the amine violet and the bisacetyl derivative bluish-white.

3 : 3′-*Dinitrodiphenylamine*.—A mixture of *m*-nitroacetanilide (5·4 g.), *m*-bromonitrobenzene (6·1 g.; 1 mol.), precipitated copper (0·1 g.), potassium iodide (0·1 g.), potassium carbonate (2·1 g.), and nitrobenzene (20 ml.) was maintained at 140° for 10 hours, then refluxed and saponified (cf. Goldberg, *loc. cit.*). Yield, 50%. Crystallisation of the product from nitrobenzene, and glacial acetic acid (1 in 8), gave orange crystals, m. p. 186·5° (corr.), fairly soluble in ether and boiling alcohol (Found: C, 55·5; H, 3·65; N, 16·5. $C_{12}H_9O_4N_3$ requires C, 55·6; H, 3·5; N, 16·2%). Unlike certain isomerides, it gave no colour in sulphuric acid with sodium nitrite, but the light yellow solution in alcohol became orange on addition of alcoholic potash. The dinitro-compound (0·2 g.) was dissolved in glacial acetic acid (5 ml.), quickly cooled, and treated with A.R. zinc needles (1·0 g.) and concentrated hydrochloric acid, drop by drop, until the solution was decolorised. The resultant solution was treated with sodium hydroxide, shaken out with ether, and the 3 : 3′-diaminodiphenylamine recrystallised; it did not depress the m. p. of a specimen made from 5 : 5′-dinitrodiphenylamine-2-carboxylic acid.

5-*Chloro*-2 : 6-*dinitroacridine* (II).—A mixture of 5 : 5′-dinitrodiphenylamine-2-carboxylic acid (7·6 g.) and phosphorus oxychloride (60 g.) was refluxed for 4 hours and distilled to dryness at 160°. The residue was cooled in a desiccator, powdered, and added to a well-stirred mixture of ice and water, kept faintly alkaline with ammonia. After filtration, the solid was dried and extracted with chloroform. The insoluble portion consisted of a mixture of 2 : 6- and 2 : 8-dinitroacridones (III and V) (9% yield) and was used to supplement the raw material in subsequent condensations. The chloroform solution gave 6·7 g. (88%) of a mixture of 5-*chloro*-2 : 6-*dinitroacridine* (principally) and the corresponding 2 : 8-dinitro-compound (IV). These were separated by repeated fractional crystallisation from benzene (1 in 40). The pure substance (II) was finally obtained in lemon-yellow needles, m. p. 200—203° (corr.), and fluoresced brightly in ultra-violet light (Found: C, 51·8; H, 2·1; N, 13·7. $C_{13}H_6O_4N_3Cl$ requires C, 51·4; H, 2·0; N, 13·8%). It is practically insoluble in water, mineral acids, or light petroleum, but dissolves in chloroform, toluene and benzene (approx. 1 in 10), and is less soluble in ether and alcohol; none of the solutions fluoresce. It is soluble in cold *N*/5-alcoholic potash to a brown solution, from which water precipitates it, and insoluble in cold 5*N*-aqueous sodium hydroxide. Both these reactions distinguish it from the corresponding acridone. In moist air, it is readily hydrolysed, and both alkaline solutions and undried organic solvents have the same action, which is most readily brought about by boiling dilute mineral acids. When it was treated for ½ hour with excess of 10% hydrochloric acid, 2 : 6-*dinitroacridone* (III) was quantitatively formed; this was washed with boiling 2% sodium carbonate solution, extracted with boiling water, dried, and dissolved (1 in 30) in 1% alcoholic potash, and the filtered solution poured into boiling *N*-hydrochloric acid. The bright yellow powder obtained (Found: C, 54·3; H, 2·6; N, 14·5. $C_{13}H_7O_5N_3$ requires C, 54·7; H, 2·5; N, 14·7%) is capable of sublimation, and is insoluble in mineral acids and all common solvents, but slightly soluble in pyridine, aniline, and molten phenol: none of its solutions show fluorescence. Aqueous alkalis dissolve only minute amounts with the production of a red-brown colour, and from these solutions mineral acids, or ammonium chloride, but not sodium chloride, reprecipitate it. The solution in alcoholic potash is wine-coloured, and excess of the solvent causes the potassium compound to be partly salted out as blood-red crystals; a dilute solution is not immediately precipitated on addition to water (distinction from the chloro-compound). 2 : 6-Dinitroacridone is not formed by the action of hot sulphuric acid on 5 : 5′-dinitrophenylamine-2-carboxylic acid, but may be obtained direct from the latter by Ullmann's acid chloride method (Ullmann, *loc. cit.*).

2 : 6-*Diaminoacridone*.—2 : 6-Dinitroacridone (5 g.) was slowly added to a boiling solution of stannous chloride (48 g.) in the same weight of fuming hydrochloric acid, and the mixture heated for ½ hour; on cooling, 8·4 g. of the ether-insoluble stannichloride were deposited. These crystals, together with a second crop, were dissolved in water and poured into sodium hydroxide solution at 0°. The precipitated amine was extracted in boiling 5% sulphuric acid, which, on filtration and cooling, deposited the insoluble sulphate. (This method of freeing an ether-insoluble amine from its stannichloride depends, first, on the low temperature of the alkali preventing the formation of metastannic acid and, secondly, on the ready hydrolysis of tin sulphate in boiling solution to an insoluble substance.) The *base*, liberated by alkali, was dissolved in alcohol, filtered, and the alcohol recovered. Yield, 75% of a bright yellow solid, which on twice crystallising from boiling water (approx. 1 in 4,000) gave greenish-yellow needles, m. p. 306° (bath at 300°), soluble in pyridine, aniline, phenol, glacial acetic acid, and alcohol (approx. 1 in 150, equally hot or cold), and sparingly soluble in benzene, nitrobenzene, toluene, and chloroform (Found for base dried at 80° : C, 66·5; H, 4·8; N, 17·6; loss at 120°, 3·5. $C_{13}H_{11}ON_3,\frac{1}{2}H_2O$ requires C, 66·7; H, 5·2; N, 17·95; H_2O, 3·8%). Unlike the 3 : 7-isomeride (cf. Bogert, *loc. cit.*), but like the white 2 : 8-isomeride, it is insoluble in 20% sodium hydroxide solution. It is diazotisable (light red solution) and then couples with β-naphthol (bright red). Aqueous and alcoholic solutions of the base fluoresce yellow-green. The fluorescence of an alcoholic solution disappears on boiling and reappears on cooling; the addition of one drop of hydrochloric acid intensifies it, but ammonia has no effect. Glacial acetic acid solutions are devoid of fluorescence. The hydrochloride is freely soluble.

2 : 6-*Diaminoacridine* (VI).—2 : 6-Diaminoacridone (0·5 g.) and *N*-hydrochloric acid (5·0 ml.) were stirred slowly on a water-bath at 80° and *N*/2-sodium hydroxide (50 ml.) was added at once, followed by 2% sodium amalgam (50 g.) during 2 hours. The temperature still being maintained, the rate of stirring was increased so as to beat air into the mixture, which after 2 hours was acidified with sulphuric acid and treated with ferric chloride (about 0·2 g.) until a blue spot test with potassium ferrocyanide was given. After a further ½ hour's heating, the mixture was brought to the boiling point, filtered, and concentrated to 40 ml., air being excluded. Concentrated sulphuric acid (4 ml.) was added and the sparingly soluble, bright red sulphate obtained was recrystallised three times from boiling water in the presence of decolorising carbon and sulphuric acid. The base, liberated in 50% yield with sodium hydroxide, repeatedly crystallised from boiling water (approx. 1 in 100), and dried in a vacuum at 100°, formed brownish-orange felted needles (yield, 23%), m. p. 213—216° (decomp.) (bath at 200°), soluble in pyridine, slightly soluble in cold water, and very soluble in alcohol, in which the 2 : 8-isomeride is far less soluble; in all other common solvents 2 : 6-*diaminoacridine* was practically insoluble (Found : N, 20·0. $C_{13}H_7N_3$ requires N, 20·1%). None of its solutions exhibit fluorescence. It has a bitter taste, stains the skin bright yellow, is slightly hygroscopic, and tends to oxidise, especially in warm air, becoming deeper in colour. The hydrochloride is readily soluble, forms a yellow precipitate with formaldehyde, and gives a violet diazo-solution which couples with β-naphthol (wine-red).

5-*Chloro*-2 : 8-*dinitroacridine* (IV).—This was isolated from the first mother-liquors of the 2 : 6-dinitro-isomeride (*v.s.*) and, purified by repeated fractional crystallisation from benzene (1 in 50), formed brownish-yellow rosettes of needles, m. p. 247—248·5° (corr.), which profoundly depressed the m. p. of the 2 : 6-dinitro-isomeride. It is soluble in the same solvents as the latter, gives the same distinguishing reactions with alkalis, and is hydrolysed by the same reagents to lemon-yellow 2 : 8-dinitroacridone (V). The latter substance exhibits physical and chemical properties qualitatively identical with those already described for its 2 : 6-isomeride. The solubility in 1% alcoholic potash is twice as great as that of the 2 : 6-isomeride, but the colours of the solutions are very similar, whereas Ullmann (*loc. cit.*) found a considerable difference in the colours of alcoholic potash solutions of the 6- and 8-nitroacridones (1- and 3- in his nomenclature). Reduction of 2 : 8-dinitroacridone by the method described for the 2 : 6-isomeride gave 2 : 8-diaminoacridone, which displayed all the properties ascribed to it in the literature, as well as the following, hitherto unrecorded : the solubility in boiling 97% alcohol is approx. 1 in 320, in boiling water, approx. 1 in 4000, the latter being suitable for recrystallisation. The aqueous solution shows a violet fluorescence whether hot or cold, but the violet fluorescence displayed in alcoholic solutions between the concentrations of 1 in 3000 and 1 in 10^7, and reaching a maximum at approx. 1 in 500,000, disappears temporarily on heating. This fluorescence is changed to intense greenish-blue by a trace of hydrochloric acid, but ammonia is without effect. In glacial acetic acid solution, the fluorescence is intense blue-green and disappears on standing. In acid solution 2 : 8-diaminoacridone gives an orange-

yellow precipitate with formaldehyde. It is diazotisable (light red solution) and then couples with β-naphthol (bright red). The sulphate consists of bright orange-yellow crystals soluble approx. 1 in 7000 in cold water and readily hydrolysed, but appreciably soluble in boiling water in the presence of a little excess acid. The 2 : 8-*dibenzylidene* derivative formed golden satiny crystals from nitrobenzene, m. p. approx. 370° (decomp.), readily hydrolysed by cold dilute acids (Found : N, 10·4. $C_{27}H_{19}ON_3$ requires N, 10·5%). The 2 : 8-*bisacetyl* derivative formed an ivory-white powder, slightly soluble in hot 60% acetic acid and insoluble in all other solvents; it does not melt below 350° (Found by the method of Phillips, *Ind. Eng. Chem. Anal. Ed.*, 1934, 321 : CH_3·CO, 27·25. $C_{17}H_{15}O_3N_3$ requires CH_3·CO, 27·8%). The 2 : 8-*bisbenzoyl* derivative, obtained by the action of benzoyl chloride on the amine in pyridine, formed a light, buff-coloured, micro-crystalline powder, insoluble in all solvents and not melting below 350° (Found : N, 9·3. $C_{27}H_{19}O_3N_3$ requires N, 9·7%). When 2 : 8-diaminoacridone (4·1 g.), suspended in aqueous sodium hydroxide (1500 ml. of 2%), was treated with sodium amalgam (400 g. of 2%) under the conditions described for the 2 : 6-isomeride, and air was beaten into the mixture for 6 hours longer, 2 : 8-diaminoacridine (proflavine base) was deposited without the necessity for the use of ferric chloride. After cooling, it was filtered off as orange-yellow needles, m. p. 277—280° (3·33 g.; 90% yield). On recrystallisation from boiling water, the m. p. rose to 281° and was not lowered by an authentic specimen of m. p. 281—282°.

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21. *The Preparation of Diaryl α-Diketones.*

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Oxidation of the nine aryl benzyl ketones now examined with selenium dioxide in acetic anhydride solution by Riley's method (compare Riley, Morley, and Friend, J., 1932, 1875; Simonsen, Evans, and Ridgion, J., 1934, 137) leads to almost quantitative formation of the corresponding α-diketones. The method thus appears to be a general one for the preparation of substituted benzils and, in view of the ready accessibility of aryl benzyl ketones (Jenkins, *J. Amer. Chem. Soc.*, 1933, **55**, 703; Jenkins and Richardson, *ibid.*, p. 1618), one of the most convenient. The yields of diaryl α-diketones previously prepared from aryl benzyl ketones by means of other oxidising agents have been much less satisfactory (Weiss, *Monatsh.*, 1919, **40**, 391; Ruggli and Reinert, *Helv. Chim. Acta*, 1926, **9**, 67; Ruggli and Jenny, *ibid.*, 1927, **10**, 228; Gomberg and van Natta, *J. Amer. Chem. Soc.*, 1929, **51**, 2238).

We have failed to confirm Weiss's (*loc. cit.*) description of 4-methylbenzil. We find that this substance melts at 31° and its structure has been established by conversion into the *r*-phenyl-*p*-tolylglycollic acid of McKenzie and Christie (J., 1934, 1074). Repeating Weiss's experiment, we have found his substance, m. p. 99—101°, obtained by hydrolysis of αα-dibromobenzyl *p*-tolyl ketone with alcohol, to be impure *p*-tolyl benzyl ketone, which is formed together with an oil containing much 4-methylbenzil. This hydrolysis therefore resembles that of αα-dibromodeoxybenzoin by water, in which benzil and deoxybenzoin are produced (Limpricht and Schwanert, *Annalen*, 1870, **155**, 68). The suspicion, at first entertained, that Weiss's substance might be *r*-*p*-toluoylphenylcarbinol arising from the monobromo-compound whose formation always accompanies that of the dibromo-compound, has revealed a more suitable method of preparation for this carbinol than those previously described (McKenzie, Martin, and Rule, J., 1914, **105**, 1583; Weissberger, Strasser, Mainz, and Schwarze, *Annalen*, 1930, **478**, 127). It is readily produced by hydrolysis of α-bromobenzyl *p*-tolyl ketone.

Experimental.

Oxidation of Phenyl Benzyl Ketone.—The following account indicates the general method employed. Phenyl benzyl ketone (4 g.; 0·02 mol.), selenium dioxide (3·4 g.; 0·03 mol.), and acetic anhydride (6 c.c.) were heated for 3—4 hours on an oil-bath at 140—150°. The liquid

was filtered from precipitated selenium, the latter washed with acetic anhydride, the filtrates poured into water, and the mixture warmed to destroy the anhydride. The solid product (4·0 g.), which contained traces of selenium and organo-selenium compounds, was boiled with animal charcoal in alcohol containing a little dilute hydrochloric acid (yield, 3·7 g. of pure benzil).*

4-Phenylbenzil.—From 8·2 g. of 4-diphenylyl benzyl ketone (Päpcke, *Ber.*, 1888, **21**, 1339) 4-phenylbenzil was obtained in similar manner. Yield, after crystallisation from methyl alcohol, 8·2 g.; m. p. 104—105° (compare Gomberg and van Natta, *loc. cit.*).

For characterisation the benzils were transformed into 5 : 5-diarylhydantoins, which are readily produced, crystallise well, and have well-defined melting points. Together with the diarylhydantoin, amounts of diarylacetylenediureide, $CO\!<\!\begin{smallmatrix}NH\cdot CAr-NH\\ NH\cdot CAr'\cdot NH\end{smallmatrix}\!>\!CO$, were produced which varied with the nature of the benzil. The last substances are therefore produced, not only in neutral media (see C. W. Porter, "Molecular Rearrangements," A.C.S. Monograph, No. 45, p. 96), but also in the presence of alkali. The preparation of 5-phenyl-5-(4'-diphenylyl)hydantoin indicates the general method employed. 4-Phenylbenzil (1·0 g.), potassium hydroxide (1·0 g.), urea (1·0 g.), and 96% alcohol (20 c.c.) were refluxed on a water-bath for 2 hours and then poured into water. The precipitated *phenyl-4-diphenylylacetylenediureide* (0·43 g.) crystallised from acetic acid in small white plates, m. p. 316—318° (Found: N, 14·9. $C_{22}H_{18}O_2N_4$ requires N, 15·1%). Saturation of the aqueous filtrate from the diureide with carbon dioxide precipitated almost pure *5-phenyl-5-(4'-diphenylyl)hydantoin* (0·70 g.), which separated from alcohol in colourless needles, m. p. 242—242·5° (Found: N, 8·45. $C_{21}H_{16}O_2N_2$ requires N, 8·5%).

4-Chlorobenzil.—Obtained from 2·3 g. of 4-chlorophenyl benzyl ketone, this *benzil* (2·4 g.) crystallised from alcohol in light yellow needles, m. p. 73° (Found: Cl, 14·2. $C_{14}H_9O_2Cl$ requires Cl, 14·5%). Oxidation with hydrogen peroxide gave a mixture of 4-chlorobenzoic and benzoic acids.

Phenyl-4-chlorophenylacetylenediureide separated from acetic acid in white micro-crystals, m. p. 339° (Found: N, 16·65. $C_{16}H_{13}O_2N_4Cl$ requires N, 17·0%), and *5-phenyl-5-(4'-chlorophenyl)hydantoin* from alcohol in white needles, m. p. 243° (Found: N, 9·6. $C_{15}H_{11}O_2N_2Cl$ requires N, 9·8%).

4-Bromobenzil.—Oxidation of 2·75 g. of 4-bromophenyl benzyl ketone (Kohler and Petersen, *J. Amer. Chem. Soc.*, 1933, **55**, 1073) gave 2·8 g. of *4-bromobenzil*, which crystallised from alcohol in yellow needles, m. p. 86·5° (Found: Br, 27·8. $C_{14}H_9O_2Br$ requires Br, 27·65%).

5-Phenyl-5-(4'-bromophenyl)hydantoin crystallised from alcohol in small white needles, m. p. 239° (Found: N, 8·5. $C_{15}H_{11}O_2N_2Br$ requires N, 8·5%).

3 : 4-Dimethylbenzil.—Oxidation of 2·3 g. of *o*-4-xylyl benzyl ketone (Wege, *Ber.*, 1891, **24**, 3540) gave 2·4 g. of this *benzil*, which crystallised from methyl alcohol in pale yellow needles, m. p. 63·5° (Found: C, 80·1; H, 5·9. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%).

The orientation of the methyl groups in the preceding aryl benzyl ketone had not been definitely established. That they have the positions now assigned was shown by oxidation of the corresponding benzil to 3 : 4-dimethylbenzoic acid. The procedure of Schönberg and Malchow (*Ber.*, 1922, **55**, 3746) was found preferable to that of Weitz and Scheffer (*Ber.*, 1921, **54**, 2327). The following account indicates the method employed in all subsequent cases. 3 : 4-Dimethylbenzil (0·5 g.) in pyridine (1 c.c.) was treated with 30% hydrogen peroxide (2 c.c.) and then with *N*-sodium hydroxide (2·5 c.c.). After heating until the solution was clear (5 minutes), acidification with hydrochloric acid precipitated the mixed acids. The benzoic acid (m. p. 121°) was removed with hot water; the residual 3 : 4-dimethylbenzoic acid, after crystallisation from hot water, melted at 165°.

5-Phenyl-5-o-4'-xylylhydantoin separated from alcohol as a white crystalline powder, m. p. 225° (Found: N, 10·0. $C_{17}H_{16}O_2N_2$ requires N, 10·0%). *Phenyl-o-4-xylylacetylenediureide* was obtained as a white powder from acetic acid, m. p. 333° (Found: N, 17·4. $C_{18}H_{18}O_2N_4$ requires N, 17·4%).

m-4-Xylyl benzyl ketone was obtained by Wege (*loc. cit.*) from *m*-xylene and phenylacetyl chloride by the Friedel–Crafts reaction and stated to undergo partial solidification on long stand-

* For complete oxidation of the aryl benzyl ketones to the corresponding benzils an excess of selenium dioxide is necessary, since the acetic anhydride employed as solvent is simultaneously oxidised. Postovsky and Lugovkin (*Ber.*, 1935, **68**, 852) have shown that the acetic anhydride is thereby largely transformed into glyoxylic anhydride. Except that an excess of selenium dioxide is required, this oxidation of acetic anhydride appears not to interfere with these preparations of diaryl α-diketones.

ing. We have found this to occur only when the *m*-xylene is contaminated with *o*-xylene and to be due to the separation of *o*-4-xylyl benzyl ketone. Pure *m*-4-xylyl benzyl ketone is a colourless oil, b. p. 202—205°/13 mm. Wege's similar observation concerning *p*-xylyl benzyl ketone is likewise explained.

2 : 4-*Dimethylbenzil*.—*m*-4-Xylyl benzyl ketone (20 g.), selenium dioxide (15 g.), and acetic anhydride (15 c.c.), after being heated for 3 hours at 150° and worked up in the usual manner, gave an oil. This was taken up in benzene, the solvent removed, and the oil heated with animal charcoal in acidified alcohol. Filtration and distillation under reduced pressure gave a yellow oil, b. p. 228°/16 mm., which formed a glass at − 60° but did not solidify (Found : C, 80·2; H, 5·8. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%). Oxidation with hydrogen peroxide gave 2 : 4-dimethylbenzoic acid (m. p. 126°) and benzoic acid.

*5-Phenyl-5-*m*-4′-xylylhydantoin* crystallised from alcohol in small needles, m. p. 269° (Found : N, 9·9. $C_{17}H_{16}O_2N_2$ requires N, 10·0%).

2 : 5-*Dimethylbenzil*.—Oxidation of *p*-xylyl benzyl ketone (8 g.) yielded an oil (7·6 g.), which solidified at − 60°. Thereafter it crystallised from alcohol in pale yellow rosettes of needles, m. p. 41° (Found : C, 80·4; H, 5·9%). Oxidation with hydrogen peroxide produced 2 : 5-dimethylbenzoic acid (m. p. 132°) and benzoic acid. *5-Phenyl-5-*p*-xylylhydantoin*, after crystallisation from alcohol, melted at 266° (Found : N, 10·1%).

2 : 4 : 6-*Trimethylbenzil*.—4·9 G. of this benzil were obtained by oxidation of mesityl benzyl ketone (4·8 g.). It crystallised from chloroform and alcohol in compact lemon-yellow crystals, m. p. 137° (Found : C, 80·8; H, 6·4. Calc. for $C_{17}H_{16}O_2$: C, 80·9; H, 6·4%). Gray and Fuson (*J. Amer. Chem. Soc.*, 1934, **56**, 2100) give m. p. 136—137°. Oxidation with hydrogen peroxide gave 2 : 4 : 6-trimethylbenzoic acid, m. p. 154°, and benzoic acid. Prolonged boiling with urea in alcoholic potash gave no diarylhydantoin.

4-*Methylbenzil*.—Oxidation of 12·6 g. of *p*-tolyl benzyl ketone gave 10 g. (theo., 13·4 g.) of a yellow oil, b. p. 219—221°/15 mm., which solidified in ether–solid carbon dioxide. It separated from alcohol at 0° in soft, pale yellow crystals, m. p. 31° (Found : C, 80·2; H, 5·4. Calc. for $C_{15}H_{12}O_2$: C, 80·3; H, 5·4%). Oxidation with hydrogen peroxide gave *p*-toluic acid, m. p. 176°, and benzoic acid.

From the reaction of 4-methylbenzil (2 g.) with urea in alkaline alcoholic solution there were isolated 0·47 g. of *phenyl-*p*-tolylacetylenediureide*, m. p. 335° after crystallisation from acetic acid (Found: N, 17·9. $C_{17}H_{16}O_2N_4$ requires N, 18·2%), and 1·82 g. of *5-phenyl-5-*p*-tolylhydantoin*, obtained as a white micro-crystalline solid from alcohol (Found : N, 10·4. $C_{16}H_{14}O_2N_2$ requires N, 10·5%).

Contrary to Weiss's statement (*loc. cit.*), 4-methylbenzil has been found to yield the corresponding benzilic acid readily on treatment with alcoholic potash. 4-Methylbenzil (2 g.), potassium hydroxide (1 g.), and 96% ethyl alcohol (10 c.c.) were refluxed together for 2 hours, the mixture was poured into water, and the filtered solution neutralised. One drop of very dilute hydrochloric acid was added, and the slight precipitate collected. After three repetitions of this process acidification precipitated *r*-phenyl-*p*-tolylglycollic acid, m. p. 127—129°, and 132° after crystallisation from chloroform–light petroleum.

Hydrolysis of αα-Dibromobenzyl p-*Tolyl Ketone*.—The dibromo-ketone (2·9 g.) was prepared by gradually adding 3·6 g. of bromine in 18 c.c. of chloroform to a boiling solution of 2 g. of *p*-tolyl benzyl ketone in 10 c.c. of chloroform and, after 1 hour, removing the chloroform and washing the crystalline residue with light petroleum. (The petroleum extracts contain a mixture of mono- and di-bromo-derivatives.) It separated from benzene–light petroleum in colourless hexagonal prisms, m. p. 128—129° (Found : Br, 43·2. Calc. for $C_{15}H_{12}OBr_2$: Br, 43·4%). When 2 g. of this material were heated for 6 hours at 160° with 12 c.c. of alcohol, the latter was entirely converted into ether and water. From the ethereal layer a semi-solid material was obtained, separable into a white crystalline solid (0·2 g.), m. p. 90—100°, and a yellow oil. Crystallised from methyl alcohol, the solid formed white needles, m. p. 110—111°, identified as *p*-tolyl benzyl ketone by mixed m. p. and by conversion into the dibromo-derivative. The yellow oil was shown to be crude 4-methylbenzil by rearrangement to *r*-phenyl-*p*-tolylglycollic acid.

α-Bromobenzyl p-*Tolyl Ketone*.—To a boiling solution of *p*-tolyl benzyl ketone (2 g.) in chloroform (10 c.c.), bromine (1·7 g.) in chloroform (10 c.c.) was added during 15 minutes. After 1 hour's refluxing, the chloroform was removed, and the residue crystallised from benzene–light petroleum. α-Bromobenzyl *p*-tolyl ketone separated in long needles, m. p. 87·5—88° (Found : Br, 27·5. Calc. for $C_{15}H_{13}OBr$: Br, 27·6%).

r-p-*Toluoylphenylcarbinol*.—1 G. of the above bromide was added, with shaking, to 0·2 g.

of sodium methoxide in 10 c.c. of methyl alcohol cooled in ice. After $\frac{3}{4}$ hour the mixture was poured into water and the oil separating was extracted with ether. Evaporation of the ether and addition of light petroleum gave a white solid. By crystallisation from aqueous methyl alcohol 0·44 g. (theo., 0·78 g.) of *r*-*p*-toluoylphenylcarbinol was obtained, m. p. 110—111° (Found: C, 79·8; H, 6·2. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%).

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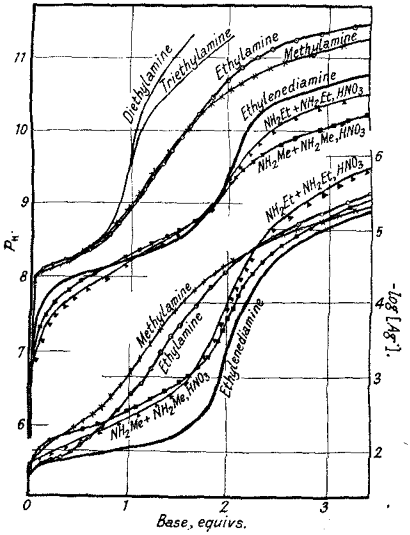
22. *Electrometric Studies of the Precipitation of Hydroxides. Part XIII. The Reactions between Silver Nitrate and Methylamine, Mono-, Di-, and Tri-ethylamine, Ethylenediamine, Aniline, and Pyridine in Solution.*

By H. T. S. BRITTON and WILLIAM G. WILLIAMS.

THIS communication reports a study of the formation of complex silver kations when various organic bases are added to a solution of silver nitrate. As might be expected, the extent to which bases precipitate silver oxide and the amounts which must be added to

FIG. 1.



effect its redissolution depend on the instability constant of the complex kation, the solubility product of silver oxide, and the dissociation constant of the organic base.

The curves in the upper section of Fig. 1 represent glass-electrode titrations at 18° of 100 c.c. of 0·02*N*-silver nitrate with 0·0896*N*-diethylamine, 0·102*N*-triethylamine, 0·09775*N*-

ethylamine, 0·0953*N*-methylamine, and 0·225*N*-ethylenediamine. A faint opalescence was soon formed in the last titration, but disappeared immediately 2 equivs. had been added. In the two titrations illustrated by the two lowest p_H curves sufficient nitrate of the base was inserted in the silver nitrate solutions so that on treatment with the respective base no precipitate appeared. In these cases, therefore, and also in that of ethylenediamine, the silver must have been held in solution in the form of complex kations: this is reflected in the titration curves by the inflexions with 2 equivs. of the bases.

The addition of di- and tri-ethylamine caused extensive precipitation of silver oxide, as indicated by the appearance of well-defined inflexions with 1 equiv. of each base. With both ethylamine and methylamine the precipitation was less: the curves have inflexions extending from 1 to 2 equivs.

The silver electro-titration curves (lower part of Fig. 1), which refer to the solutions and titrants of the same concentrations as above, have similar characteristics. The ethylenediamine curves bring out clearly the fact that the complex salt involves one molecule of the base, $AgNO_3 + C_2H_4(NH_2)_2 \longrightarrow Ag[C_2H_4(NH_2)_2]NO_3$. [The complex kation is usually represented by AgEn˙ (see, however, Traube, *Ber.*, 1911, **44**, 3320).] The proportion of silver oxide precipitated at various stages of the titrations was determined by precipitation of the silver in solution as chloride. To 100 c.c. of 0·02*N*-silver nitrate various amounts of base were added, mechanically shaken for some time at room temperature, and the silver in the liquid phase estimated. The results obtained are given in Table I.

TABLE I.

100 *C.c. of* 0·02N-*silver nitrate* + x *c.c. of* 0·0956N-*methylamine.*

x, c.c.	10	15	20	25	30	40	45	50	60
$NH_2Me/AgNO_3$	0·48	0·72	0·96	1·19	1·43	1·91	2·15	2·49	2:87
Ag pptd., % (obs.)	46·1	66·6	78·3	75·9	65·3	42·4	34·8	26·5	14·5
,, (calc.)	47·5	57·1	78·4	—	64·7	38·3	—	21·5	14·8

100 *C.c. of* 0·1N-*silver nitrate* + x *c.c. of* 0·5087N-*methylamine.*

x, c.c.	5	10	15	20	25	30	35	40	45	48
$NH_2Me/AgNO_3$	0·25	0·51	0·76	1·02	1·27	1·53	1·78	2·03	2·29	2·54
Ag pptd., % (obs.)	25·4	46·5	69·8	77·7	67·3	46·0	29·9	17·3	9·2	5·0
,, (calc.)	25·5	48·7	70·2	79·7	73·6	50·2	30·2	14·8	—	—

100 *C.c. of* 0·02N-*silver nitrate* + x *c.c. of* 0·0973N-*ethylamine.*

x, c.c.	10	15	20	25	30	35	40	45	50
$NH_2Et/AgNO_3$	0·48	0·73	0·97	1·21	1·46	1·70	1·94	2·19	2·43
Ag pptd., % (obs.)	41·0	56·7	66·2	60·4	49·0	33·2	21·3	12·5	4·4
,, (calc.)	44·6	60·7	67·3	—	56·9	36·9	—	12·2	—

100 *C.c. of* 0·1N-*silver nitrate* + x *c.c. of* 0·4676N-*ethylamine.*

x, c.c.	5	10	15	20	25	30	35	40	45	48
$NH_2Et/AgNO_3$	0·23	0·47	0·70	0·94	1·17	1·40	1·64	1·87	2·10	2·22
Ag pptd., % (obs.)	20·3	38·8	55·3	65·7	63·2	51·1	34·3	15·7	5·9	2·7
,, (calc.)	22·6	43·0	59·2	67·3	—	60·2	37·6	16·9	—	—

100 *C.c. of* 0·02N-*silver nitrate* + x *c.c. of* 0·0896N-*diethylamine.*

x, c.c.	5	10	15	20	25	30	40	60	80
$NHEt_2/AgNO_3$	0·22	0·45	0·67	0·90	1·12	1·34	1·79	2·69	3·59
Ag pptd., %	22·4	45·0	66·4	85·1	94·2	96·0	76·6	60·8	41·9

100 *C.c. of* 0·02N-*silver nitrate* + x *c.c. of* 0·112N-*triethylamine.*

x, c.c.	5	10	15	20	25	30	40	60	80
$NEt_3/AgNO_3$	0·26	0·51	0·77	1·02	1·27	1·53	2·04	3·06	4·08
Ag pptd., %	22·9	51·0	75·0	91·6	97·5	97·5	95·0	93·0	91·6

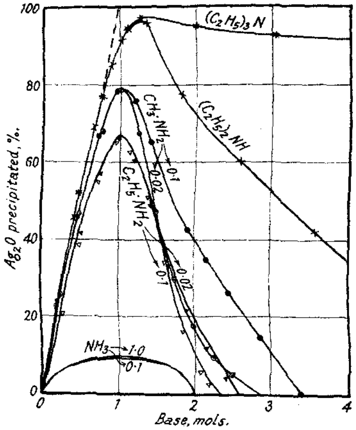
The results are plotted in Fig. 2, in which are also curves showing the percentage of silver oxide precipitated when 0·1*N*- and 1·0*N*-silver nitrate solutions are treated with ammonia (see Britton and Wilson, *J.*, 1933, 1050). The broken line represents the normal precipitation of silver oxide with sodium hydroxide. Unlike ammonia, none of the organic bases causes the silver oxide to redissolve when 2 mols. of base per mol. of silver nitrate have been added. Reychler (*Ber.*, 1883, **16**, 990) and Herz (*Z. anorg. Chem.*, 1910, **67**, 248) considered the ratio 2 : 1 to indicate formation of the complex kation, $Ag(NH_3)_2^{\cdot}$, but, as the following considerations show, such a ratio is fortuitous in that the precise ratio depends on the three factors mentioned on p. 96.

When a base, B, is added to silver nitrate, two reactions occur simultaneously: (i) the partial precipitation of silver oxide, (ii) conversion of some silver nitrate into the complex nitrate, AgB_2NO_3. These two reactions bring into play the equilibria $AgB_2^{\cdot} \rightleftharpoons Ag^{\cdot} + 2B$, $B + H_2O (= BH{\cdot}OH) \rightleftharpoons BH^{\cdot} + OH'$, and AgOH (solid) $\rightleftharpoons$ AgOH (dissolved) $\rightleftharpoons$ $Ag^{\cdot} + OH'$, which are governed by the expressions $K_1 = \frac{[Ag^{\cdot}][B]^2}{[AgB_2^{\cdot}]}$; $K_b = \frac{[BH^{\cdot}][OH']}{[B]}$; $L = [Ag^{\cdot}][OH']$,

whence $$K_1 . K_b^2/L^2 = [BH^{\cdot}]^2/[Ag^{\cdot}][AgB_2^{\cdot}] \quad (1)$$

and $$K_1 . K_b/L = [BH^{\cdot}][B]/[AgB_2^{\cdot}] \quad (2)$$

FIG. 2.



Equation (1) is applicable particularly to the first stage of the reaction of the base with silver nitrate, *i.e.*, when there is an appreciable silver-ion concentration originating from any unattacked silver nitrate (Case I), and equation (2) refers to the second stage where some of the added base has failed to react, either in precipitating silver oxide or in forming the complex salt, AgB_2NO_3 (Case II). From a knowledge of the three constants involved, it is possible to calculate the extents to which the base has reacted in (*a*) precipitating silver oxide and (*b*) complex formation. Thus, let the original concentration of silver nitrate be c, and the total concentration of added base $2a$; of the silver nitrate reacted upon, suppose a fraction, x, yielded an equivalent quantity of silver oxide.

Case I.

$$2axBH{\cdot}OH + 2axAgNO_3 = 2axB,HNO_3 + 2axAgOH$$
$$2a(1-x)B + a(1-x)AgNO_3 = a(1-x)AgB_2NO_3.$$

The complete ionisation of B,HNO_3, AgB_2NO_3, and any unattacked $AgNO_3$ being assumed, it follows that $[BH^{\cdot}] = 2ax$, $[AgB_2^{\cdot}] = a(1-x)$, and $[Ag^{\cdot}] = \{c - a(1-x) - 2ax\}$, whence $K_1 . K_b^2/L^2 = 4ax^2/(c - a - ax)(1-x)$ from which the fraction of silver oxide precipitated, *viz.*, $2ax/c$, can be calculated.

Case II.

$$2c(1-x)B + c(1-x)AgNO_3 = c(1-x)AgB_2NO_3$$
$$xcBH{\cdot}OH + xcAgNO_3 = xcB,HNO_3 + xcAgOH$$
$$[BH^{\cdot}] = xc,\ [B] = \{2a - xc - 2c(1-x)\},\ [AgB_2^{\cdot}] = c(1-x)$$

Hence $K_I . K_b/L = x(2a + xc - 2c)/(1 - x)$ and the fraction of oxide precipitated is xc/c. With $L_{AgOH} = 1{\cdot}33 \times 10^{-8}$ (Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 539) and with the dissociation constants of the bases and instability constants of the complex kations found by us in Part XII (J., 1935, 796), the percentages of silver precipitated as oxide were calculated and are recorded in Table I. In view of the approximations involved, the agreement between the calculated and the observed results is satisfactory. This is also the case in regard to the extent of precipitation from silver nitrate solutions with ammonia as found by Britton and Wilson (J., 1933, 1050). With $p_{K_{NH_4OH}} = 4{\cdot}72$ and $p_{K_{Ag(NH_3)_2^\cdot}} = 7{\cdot}70$, calculation shows that 7·83, 9·18, and 7·83% of the total silver nitrate should be precipitated with 0·5, 1·0, and 1·5 equivs. of ammonia respectively, whereas the proportions found were 7·68, 8·83, 7·81% and 7·81, 9·68, 7·95% from $0{\cdot}1M$- and $1{\cdot}0M$-silver nitrate respectively. For the methylamine calculations, $p_{K_{NH_2Me}} = 3{\cdot}43$ and $p_{K_{Ag(NH_2Me)_2^\cdot}} = 7{\cdot}10$ were adopted, and for those with ethylamine, $p_{K_{NH_2Et}} = 3{\cdot}40$ and $p_{K_{Ag(NH_2Et)_2^\cdot}} = 7{\cdot}70$.

The p_H values (Fig. 1) of the solutions after the silver oxide had dissolved in both the methylamine and the ethylamine titrations indicate buffer action which must have been caused by the presence of the nitrates of these bases. The existence of these salts shows that the silver nitrate could not have been quantitatively converted into the complex salts, AgB_2NO_3.

As it is probable that, in those titrations which involved the redissolution of silver oxide, a state of equilibrium was not immediately reached, several series of solutions containing various excesses of the organic bases were prepared, mechanically shaken in light-proof bottles for 24 hours at room temperature, and their silver- and hydrogen-ion concentrations determined by means of the silver and the glass electrode respectively. The silver electrodes were prepared by electrodepositing coarsely crystalline silver on silver rods. The glass cell *E.M.F.*'s were measured by means of an electrometer–triode valve and a sensitive galvanometer. The normal electrode potential of the silver electrode was 0·801 volt (N-H = 0). Table II gives the results obtained; each solution was $0{\cdot}02N$ with respect to silver nitrate; the concentration of methyl- and ethyl-ammonium nitrate (sections *b* and *d* respectively) entirely prevented the precipitation of silver oxide.

From the p_H values and the *E.M.F.* data, the instability constants, K_I, of the complex kations were calculated. As methylamine and ethylamine are both appreciably ionised, it is necessary, in order to calculate [B], to deduct the concentration $[BH^\cdot]$ from the concentration of the base in excess of the 2 mols. going to form the complex kation. On the assumption that $[BH{\cdot}OH] = [B]$, we have $[BH^\cdot] = [OH'] = K_w/[H^\cdot]$.

TABLE II.

Cell: $Ag\,|\,0{\cdot}02N\text{-}AgNO_3 + xN\text{-}NH_2Me$ (or NH_2Et) | satd. $KNO_3\,|\,N$-Calomel.

(*a*) Solutions: $0{\cdot}02N\text{-}AgNO_3 + xN\text{-}NH_2Me$.

NH_2Me, x.	$\frac{[NH_2Me]}{[AgNO_3]}$.	p_H at 17·5°.	$10^3[OH']$.	*E.M.F.*	$-\log [Ag^\cdot]$.	$K_I \times 10^8$.
0·2276	11·38	11·70	3·5	0·111 (16°)	7·10	12·9
0·9108	45·54	12·26	12·9	0·029	8·53	11·9
1·1280	56·90	12·30	14·0	0·016	8·76	11·1

Mean $K_I = 12{\cdot}0 \times 10^{-8}$

(*b*) Solutions: $0{\cdot}02N\text{-}AgNO_3 + 0{\cdot}063N\text{-}NH_2Me,HNO_3 + xN\text{-}NH_2Me$.

0·0814	4·07	10·76	—	0·168 (19°)	6·03	7·92
0·1017	5·08	10·92	—	0·148 (19°)	6·46	7·58
0·1220	6·10	11·01	—	0·137 (19°)	6·58	8·71

Mean $K_I = 8{\cdot}1 \times 10^{-8}$

(*c*) Solutions: $0{\cdot}02N\text{-}AgNO_3 + xN\text{-}NH_2Et$.

NH_2Et, xN.	$\frac{[NH_2Et]}{[AgNO_3]}$.	p_H at 17·5°.	$10^3[OH']$.	*E.M.F.*	$-\log [Ag^\cdot]$.	$K_I \times 10^8$.
0·2123	10·62	12·11	9·19	0·072 (18°)	7·72	2·63
0·4246	21·23	12·315	14·6	0·034	8·38	2·95
0·8494	42·46	12·415	18·4	0·000	8·97	3·24
1·698	84·92	12·57	26·0	−0·035	9·58	3·44

Mean $K_I = 3{\cdot}1 \times 10^{-8}$

(*d*) Solutions: $0{\cdot}02N\text{-}AgNO_3 + 0{\cdot}1013N\text{-}NH_2Et,HNO_3 + xN\text{-}NH_2Et$.

0·09020	4·51	10·75 *	—	0·130	6·69	2·56
0·1082	5·41	10·88 *	—	0·113	6·98	2·40
0·1173	5·86	10·98 *	—	0·106	7·12	2·23

* At 18°. Mean $K_I = 2{\cdot}4 \times 10^{-8}$

The values of the instability constant for $Ag(NH_2Me)_2^{\cdot}$ [Table II (*a*)] tend to decrease as the concentration of free base increases, whilst those given in Table II (*b*) are still smaller. The lower values, indicating increased stability of the complex kation, are believed to be the result of the repression of ionisation of the excess of base, in the first case by the greater concentrations of methylammonium ions owing to the added nitrate, and in the second by the relatively high concentration of hydroxyl-ions originating from the complex base. Euler (*Ber.*, 1903, **36**, 1854, 2878) obtained values ranging from $1{\cdot}19 \times 10^{-7}$ to $2{\cdot}5 \times 10^{-7}$ for the methylamine complex kation.

The ethyl base shows a similar behaviour [Table II, (*c*) and (*d*)]. The lower value, $2{\cdot}4 \times 10^{-8}$, compares satisfactorily with the values, $1{\cdot}88 \times 10^{-8}$ and $2{\cdot}13 \times 10^{-8}$, obtained from the aqueous ethylamine solutions of silver oxide. The difference in the stability of the complex methylamine and ethylamine kations is apparent from the relative proportions of the two bases required to bring silver oxide into solution as shown in Fig. 2.

The data in Table III are derived from electrometric titrations of solutions containing ethylenediamino-, dianilino-, and dipyridino-silver ions in the presence of various amounts of the respective bases. The well-defined inflexion in the ethylenediamine curve (Fig. 1) shows the complex kation to be quite stable. The mean "instability constant," $2{\cdot}0 \times 10^{-7}$, agrees with that of the kation which ionises from the complex base, [Ag en]OH, *viz.*, $1{\cdot}15$—$1{\cdot}44 \times 10^{-7}$.

If aniline and pyridine did not enter into complex formation with silver ions, then, despite their weakness as bases, they should, when added in sufficient excess to silver nitrate solution, be able to set up p_H values which would cause the precipitation of some silver oxide. Complex kations, however, are formed, and consequently no silver oxide is precipitated. This will be seen from the diminished silver-ion concentrations recorded in Table III, (*b*) and (*c*). As the relatively large values of K_I (last columns) show, the complex kations are much less stable than any of the other kations investigated in this paper.

TABLE III.

Electrometric titrations (glass and silver electrodes) of 100 c.c. of $0{\cdot}02N$-$AgNO_3$ *with various organic bases.*

(*a*) Ethylenediamine ($0{\cdot}2250N$); 18°.

Base, c.c.	$\frac{1}{2}[C_2H_4(NH_2)_2]$ / $[AgNO_3]$	p_H.	$10^4[OH']$.	*E.M.F.**	$-\log[Ag^{\cdot}]$.	$K_I \times 10^7$.
40	4·50	10·87	6·92	0·192	5·63	1·52
60	6·75	11·08	8·91	0·165	6·10	2·18
80	9·00	11·20	11·75	0·147	6·41	2·06
90	10·10	11·25	13·20	0·141	6·51	2·07
						Mean $K_I = 2{\cdot}0 \times 10^{-7}$

(*b*) Aniline ($0{\cdot}3534N$); 17°.

Base, c.c.	$[C_6H_5{\cdot}NH_2]$ / $[AgNO_3]$	p_H.	*E.M.F.**	$-\log[Ag^{\cdot}]$.	$K_I \times 10^4$.
50	8·84	7·63	0·322	3·39	2·51
70	12·35	7·72	0·312	3·57	2·85
80	14·13	7·75	0·308	3·64	3·75
100	17·62	7·79	0·301	3·77	4·58
				Mean K_I =	$3{\cdot}4 \times 10^{-4}$

(*c*) Pyridine ($0{\cdot}5834N$); 18°.

Base, c.c.	$[C_5H_5N]$ / $[AgNO_3]$	p_H.	*E.M.F.**	$-\log[Ag^{\cdot}]$.	$K_I \times 10^4$.
30	13·47	8·50	0·275	4·18	3·80
50	19·45	8·72	0·246	4·70	3·55
70	24·03	8·83	0·230	4·97	3·63
90	27·64	8·92	0·218	5·19	3·47
				Mean K_I =	$3{\cdot}6 \times 10^{-4}$.

* Cell of same type as in Table II.

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23. *Some Kinetic Consequences of Complex Formation in Solution.*

By E. A. Moelwyn-Hughes and Albert Sherman.

Experiment shows that the influence of a solvent on the mechanism of a chemical change proceeding in its presence is specific, having a magnitude dependent on the properties of the solute and solvent molecules. It is the object of this paper to classify the various types of solvent action, for which purpose we require a knowledge of the different kinds of intermolecular forces which are hypothetically possible. The solvent effect can be formulated quantitatively in certain simple cases.

Where the topics of discussion coincide, our conclusions are in harmony with those of Nathan and Watson (J., 1933, 890, 1248) and of Waters (*ibid.*, p. 1551).

Classification of Chemical Bonds.—The occurrence of a chemical reaction always entails the making or breaking of a bond, and very often two such changes take place simultaneously. A classification of chemical reactions should thus constitute a logical corollary to any scheme of bond classification. We outline below the accepted scheme of bond classification, admitting (Lennard-Jones and Sherman, Reports of the London Physical Society, 1935) that it is too idealistic, because, in practice, no bond is entirely of one type.

A. *Homopolar bonds.* That the homopolar or covalent bond (*e.g.*, H–H, C–H) is due to a pair of electrons, was suggested empirically by Lewis in 1915. The nature of the interaction has been understood only with the recent advent of quantum mechanics. It is noteworthy that almost all the quantum-mechanical treatments of valency have been confined to the homopolar bond (for review, see van Vleck and Sherman, *Rev. Mod. Physics*, 1935, 7, 167).

B. *Electrostatic attractions.* The three sources of electrostatic attractions are ions, permanent dipoles, and induced dipoles. Electrostatic attractions arise from all possible interactions in pairs.

1. Ion–ion bond (*e.g.*, $Na^{\cdot}Cl'$ in the sodium chloride crystal; for summary, see J. Sherman, *Chem. Reviews*, 1933, 11, 93). The energy of this bond is due to the Coulomb attraction between two ions of opposite charge.

2. Dipole–dipole bond (*e.g.*, intermolecular compounds, such as are formed between ether and chloroform $(C_2H_5)_2\overrightarrow{O}$, $\overrightarrow{HC}Cl_3$). The Coulomb attraction between two molecules, each of which has a permanent dipole, is responsible for this bond. The most familiar example is afforded by the association of alcohols, but numerous instances of the behaviour described parenthetically above are also known. It will be shown that they are of importance in the study of the kinetics of reactions in solutiou.

3. Induced dipole–induced dipole bond. The forces operating here are Coulomb forces between dipoles induced in neutral atoms or molecules. They are relatively small in magnitude, and give rise to bonds so weak that the compounds are largely dissociated except at low temperatures. These so-called van der Waals forces account for the liquefaction of the rare gases and for the existence of the molecules Hg_2 and O_4.

4. Ion–dipole bond. The Coulomb attraction between an ion (*e.g.*, $Cu^{\cdot\cdot}$) and a molecule possessing a permanent dipole (*e.g.*, NH_3) results in the formation of compounds such as the tetramminocupric ion, $Cu(NH_3)_4^{\cdot\cdot}$. The relation between the bond so formed and the co-ordinate link will be discussed later.

5. Ion–induced dipole bond. The presence of an ion may induce a dipole in a molecule which is otherwise non-polar; and the interaction between the ion and the induced dipole gives rise to an attractive force which makes compound formation possible. For purposes of discussion, we may consider the stability of the tri-iodide ion (I'_3) as due, in part, to the attraction between the iodide ion and the dipole which it induces in the iodine molecule. The example is not a clear-cut one, because there is some doubt as to whether the iodine molecule in water is really non-polar. The ion–induced dipole bond is weaker than, and is always superimposed upon, the ion–dipole bond.

6. Dipole–induced dipole bond. This c[illegible]e only in that the dipole is induced by a permanent dipol[illegible]mation of the

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hydrates of the rare gases and of the halogens affords evidence for the existence of this type of bond.

The six types of electrostatic attraction discussed here are effective at relatively great separations; when the ions, dipoles, or induced dipoles are brought close together, strong repulsive forces come into effect. The interplay between attractive and repulsive forces thus gives rise to six types of bond. The magnitudes of the attractive forces are inversely proportional to the dielectric constant of the medium; hence we expect all the six bonds to be weaker in solution than in the gas phase. Nevertheless, atoms, molecules, or ions which are held together by quite small forces may form complexes which are of great importance in determining the course of chemical change.

Chemical Reactions involving the Rupture or Formation of Homopolar Bonds in Un-ionised Molecules.—The main contribution to the energy of the homopolar bond arises from a non-classical resonance, and is usually of such magnitude that we can anticipate the bond to be largely uninfluenced by a solvent environment. The potential energy of a diatomic molecule is known to be represented by an equation of the Morse type, *viz.*,

$$V(r) = D'\{e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where D' is the strength of the bond (including zero-point energy), a is a constant, and r_0 is the equilibrium separation of the nuclei. The velocity of chemical change, in general, depends on the attainment of a certain minimum potential energy, characteristic of the reacting system, and on the probability of transformation of the critical configuration, towards the formation of which the energy has been expended. Our knowledge of such probabilities is meagre, and the phrase at present is little more than a confession of ignorance. But the critical energy can often be computed in a satisfactory manner; its magnitude is dependent on the magnitude of the various D' terms involved in the reaction. Eyring and Polanyi's method of calculating the energy of activation shows that, provided an ionic mechanism does not intervene, the influence of the solvent upon the energy of activation is not very great. This conclusion harmonises with the somewhat scant experimental information (cf. Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1933). As far as it is possible to generalise, it may be said that reactions which do not involve an ion on either side of the chemical expression are less sensitive to solvent influences than those in which ions are produced or consumed. For instance, nitrogen pentoxide, chlorine monoxide, and pinene decompose at the same rate in the gas phase as in certain solvents (*op. cit.*, p. 51); the Beckmann transformation (Chapman, J., 1934, 1550) and certain catalysed mutarotations (*op. cit.*, p. 229) proceed in solution by the same mechanism as would be predicted for their behaviour in gases; the elimination of nitrogen from diazonium halides is largely insensitive to a change in the solvent medium (*op. cit.*, p. 157); and the decomposition of nitrous acid is unaffected by drastic changes in the ionic environment (*op. cit.*, p. 201). All these changes can be formulated as occurring by the breaking and making of essentially homopolar bonds, in the absence of ionic intervention. Conversely, the decomposition of triazole compounds (*op. cit.*, p. 133) and of carboxylic acids (*op. cit.*, p. 166) is influenced by a change in the solvent medium, and it may be concluded that electrostatic influences due to the solvent atmosphere have been superimposed on the chemical reaction proper.

Reactions between Two Ions in Solution.—It has been pointed out (*op. cit.*, p. 172) that there exists a fundamental distinction between true ionic reactions and reactions occurring between charged particles. Failure to recognise the distinction has led to some confusion. True ionic reactions have been defined as those wherein the attractive forces are solely the Coulomb influence between the ions, *e.g.*, the formation of the sodium chloride ion-pair in water

$$Na^+ (aq.) + Cl^- (aq.) \longrightarrow (Na^+, Cl^-) \text{ ion-pair}$$

With such reactions alone is it logical to introduce the Debye–Hückel expression for the activity into the general equation for the velocity of a bimolecular reaction proceeding by way of an intermediate complex. No data are available on this type of reaction. The formation of ion-pairs is known to proceed rapidly, but not necessarily instantaneously,

because, if the sum of the ionic solvation energies exceeds the crystal energy, the reactions will be endothermic, and may involve considerable activation. The physical reason for the necessity of activation is that the formation of an ion-pair requires the partial removal of the solvation shells. With an activation energy of the order of magnitude of the equipartition value, it would be necessary to work with concentrations of the order of magnitude of 10^{-14} g.-mol./l. in order to follow the course of reaction by ordinary methods. The method of Hartridge and Roughton, however, may prove to be helpful in the study of true ionic reactions, since a half-life of 10^{-3} sec. can be measured by its aid, and correspondingly higher concentrations of reactants could be employed. von Halban and Eisner (*Helv. Chim. Acta*, 1935, **18**, 724) have recently applied this technique to the study of fast reactions, both inorganic and organic. Their estimated values of the activation energy agree with the conclusions of this paragraph.

The simplest ionic reactions which have hitherto been examined are shown below. They refer to aqueous solutions (for more detailed information, see "The Kinetics of Reactions in Solution," pp. 37, 218, and 220). All three reactions take place between ions which have charges of the same sign, so a portion of the activation energy must be expended in overcoming the Coulomb repulsion between the ions. The energy required

Ionic Reactions.

Reaction.	Observed energy of activation (cals./g.-mol.).
(1) $ClO' + ClO' \longrightarrow Cl' + ClO_2'$	22,500
(2) $AsO_3''' + TeO_4'' \longrightarrow AsO_4''' + TeO_3''$	14,400
(3) $Sn^{\cdot\cdot} + 2Fe^{\cdot\cdot\cdot} \longrightarrow Sn^{\cdot\cdot\cdot\cdot} + 2Fe^{\cdot\cdot}$	28,200

to bring an ion of charge $z_A e$ up to a distance r_0 from a second ion of charge $z_B e$, in a medium of dielectric constant D, is

$$\varepsilon = z_A z_B e^2 / D r_0 \qquad (2)$$

With r_0 in Å., $\varepsilon = 329{\cdot}7 z_A z_B / D r_0$ kg.-cals./mol.

If, *e.g.*, $z_A = z_B = 2$, $r_0 = 2$ Å., and $D = 80$, ε becomes 8,260 cals.; hence, the interionic repulsion accounts for a considerable fraction of the activation energy. However, none of these reactions can be regarded as a true ionic reaction. Examples 1 and 2 obviously involve the breaking of covalency bonds. Example 3 is *prima facie* the most appropriate case to examine, because it involves a change in electrovalency without a change in covalency. Recent work, however, has shown that the reaction is kinetically complicated (Robinson and Law, *Trans. Faraday Soc.*, 1935, **31**, 899). The velocity constants given by experiment refer, not to the step written in the above table, but to some intermediate stage in the total reaction, which bears many of the distinguishing features of a chain reaction, though it has not yet been viewed in this light.

Such data as are available, from *E.M.F.* and conductivity measurements, suggest that the formation of ion-pairs, although a rapid process, may be the rate-determining step in several chemical processes. For example, the processes subsequent to the following reactions

$$NEt_4^+ \text{ (solvated)} + \text{Picrate}^- \text{ (solvated)} \longrightarrow [NEt_4^+, \text{Picrate}^-] \text{ (ion-pair)}$$
$$H^+ \text{ (hydrated)} + CO_3^{--} \text{ (hydrated)} \longrightarrow [H^+, CO_3^{--}] \text{ (ion-pair)}$$

which are crystallisation and the formation of a covalent link respectively,

$$[NEt_4^+, \text{Picrate}^-] \text{ (ion-pair)} \longrightarrow NEt_4 \text{ Picrate (crystalline)}$$
$$[H^+, CO_3^{--}] \text{ (ion-pair)} \longrightarrow HCO_3^- \text{ (hydrated)}$$

may well proceed rapidly in comparison with the first stage, since the subsequent stage depends only on the transference of an electron, whereas the primary stage, as stated above, involves partial desolvation.

Reactions between Two Dipoles in Solution.—Molecular complexes, long known to chemists, have recently gained new prominence because the magnitude of the dielectric constant of dilute solutions cannot be interpreted without postulating their existence,

We are here concerned with the relation between the energy of formation of such complexes and the velocity of the relevant reactions.

The potential energy of two molecules held together in a head-on position by the mutual interaction of two dipoles (μ_A and μ_B) in a medium of unvarying dielectric capacity D is

$$\varepsilon = 2\mu_A\mu_B/Dr_0^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

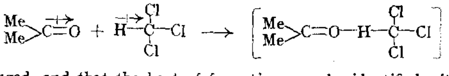
With r_0 in Å., and μ in Debye units, $\varepsilon = 28{\cdot}9\ \mu_A\mu_B/Dr_0^3$ kg.-cals./mol.

We are usually concerned with permanent moments ranging in magnitude from about 0·2 to about 3 (Debye units), and with equilibrium separations (r_0) of 1—4 Å. in media where D may have any value from 2 to 80. Hence ε lies within the approximate limits of 200 and 15,000 cals./g.-mol.

Complexes formed with the evolution of only 200 cals. can obviously not be regarded as stable at ordinary temperatures, although they may be kinetically influential. The next most stable type of complex corresponds to that postulated by Debye, where the approach is not head-on, but broad-side on, thus ⇅. Sakurada (*Z. physikal. Chem.*, 1935, *B*, **28**, 104) found the exothermic heat of formation of double molecules of phenyl halides in carbon tetrachloride solution to vary from 1,078 to 1,714 cals.; and, although there is some force in the criticism of Heitet and Dumont (*ibid.*, **29**, 15), Sakurada's values are certainly correct as regards order of magnitude. These associated compounds are fairly stable at room temperatures, but their exothermicity is scarcely large enough to constitute an important factor in determining the reactivity of the phenyl halides, where fairly large energies of activation are usually found (cf. the discussion above on the influence of solvent atmosphere on the strength of the covalent bond).

The heats of formation of complexes formed between trinitrobenzene and dibenzyl, tolan, and stilbene, vary from 600 to 3,170 cals. (Briegleb and Kambeitz, *ibid.*, 1934, **27**, 161). The energy of association of a series of seven alcohols ranges from 5,000 to 5,900 cals. in hexane solution, and from 3,400 to 4,000 cals. in benzene solution (Wolf, Pohlke, and Wehago, *ibid.*, 1935, **28**, 1). The magnitude of these energy terms, and the fact that they are independent of the nature of the alcohol, are consistent with the idea that the complexes are formed by the mutual action of two solute dipoles.

The vapour pressure, viscosity, and mutual solubility of acetone–chloroform mixtures are anomalous, in the sense that they bear no apparent relation to the composition of the mixture and to the individual properties of its components. The mixed solvent has also an anomalous effect on the velocity of reactions which proceed in it. Assuming the vapour pressure of each species to be proportional to the molar fraction in the condensed phase, Schulze (*ibid.*, 1919, **93**, 370) determined the equilibrium constant $K = n_1n_2/n_{1,2}$ at various temperatures. Applying the van't Hoff relation, we find that the postulated complex is formed exothermically, with $Q = 4{,}070$ cals. Let us assume that the complex is formed by the head-on union of the two dipoles ($\mu_{COMe_2} = 2{\cdot}75$; $\mu_{CHCl_3} = 1{\cdot}05$), that the moments



remain unchanged, and that the heat of formation may be identified with the mutual electrostatic potential energy of the system. Equating Q to $2\mu_A\mu_B/Dr_0^3$, we find $r_0 = 1{\cdot}0$ Å., which is in good agreement with the accepted separation of the hydrogen and the oxygen nucleus in most compounds.

The formation of a similar complex between ethyl ether and chloroform has been postulated by McLeod and Wilson (*Trans. Faraday Soc.*, 1935, **31**, 596), who determined the heat of reaction calorimetrically. The exothermicity is 6,070 cals./g.-mol. The dielectric constant of a mixture of 50% ether + 50% chloroform is 5·58 (Philip, *Z. physikal. Chem.*, 1897, **24**, 18). With $\mu_{Et_2O} = 1{\cdot}32$ and $\mu_{CHCl_3} = 1{\cdot}05$, we find $r_0 = 1{\cdot}05$ Å., which again is a reasonable value.

More extensive, if less accurate, information is available relating to complexes formed between nitro-compounds and hydrocarbons, and between nitrogen bases and alkyl and

aryl halides. We confine attention to the latter class, and quote but two illustrative examples from the abundant data given by Bramley (J., 1916, **109**, 11, 434). The heat of reaction, calculated from the equation $d \log_e K/dT = Q/RT^2$, using the experimental values of the equilibrium constant K, are shown in Table I. The fall in Q may be due to error in experiment or in the computation of K. It may equally well be genuine, indicating the omission of relevant factors, such as the temperature variation of the viscosity. The freezing-point curves of these mixtures show compound formation at equimolecular proportions. A 1 : 1 compound also separates in the case of *o*-chlorophenol with aniline and

TABLE I.

Heats of Formation of Intermolecular Complexes.

Quinoline and *o*-chlorophenol.			Pyridine and *o*-chlorophenol.		
Temp.	K.	Q.	Temp.	K.	Q.
60°	0·014		40°	0·0236	
		13,300			9,400
80	0·043		60	0·0670	
		13,300			8,100
110	0·189		80	0·134	
		10,800			7,600
150	0·712		110	0·313	

with dimethylaniline. Similarly, *o*-cresol and pyridine give only a 1 : 1 eutectic, but phenol and pyridine give a complex $C_5H_5N,2C_6H_5{\cdot}OH$. The behaviour is fairly general, and there is no reason to dispute that its origin is to be traced to the dipole–dipole attraction under discussion.

In considering the effect of molecular compounds upon the velocity of bimolecular reactions in liquid systems, we may first re-examine the results of Lowry and Traill (*Proc. Roy. Soc.*, 1931, *A*, **132**, 398) upon the mutarotation of beryllium benzoylcamphor under the influence of catalysts in various solvents. In carbon tetrachloride solution, the reaction is kinetically very simple: with catalysts such as cresol, pyridine, and alcohol, catalytic coefficients are found which agree with those calculated by making the usual assumptions about collision frequencies. The α- and the β-form of the reactant have equal stability in carbon tetrachloride and in hexane, but in chloroform solution the symmetrical equilibrium is displaced, indicating, as the authors point out, that the solvent now combines with both forms, but preferentially. The lessened catalytic activity of pyridine in chloroform, as compared with carbon tetrachloride, has been quantitatively ascribed to the presence of a complex, which, moreover, has been isolated in the form of a crystalline solvate with two molecules of chloroform.

We next consider the reactions between nitrogen bases and alkyl or aryl halides in various solvents. Their velocities are usually lower than those calculated by means of the equation

$$k = \sigma_{1,2}^2\{8\pi kT(1/m_1 + 1/m_2)\}^{\frac{1}{2}} . e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and many attempts have been made to account for this apparent slowness. These have all been based on the assumption that the critical increment (E_A) as given by the Arrhenius equation is a true measure of the activation energy. In a general review of bimolecular reactions in solution (Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 260) it was pointed out that these "observed critical increments are false, in the sense that, by some unknown mechanism, they have been depressed from their normal values." The interaction of the dipole of either reactant with the solvent seems to supply the missing mechanism. The reaction scheme can be formulated in the familiar way by assuming that the net change $A + B \longrightarrow AB$ proceeds *via* the reversible formation of a complex of either A or B with the solvent, S, say,

$$A + S \rightleftharpoons AS; \; K = [AS]/[A][S] = We^{+Q/RT}$$

whence it follows that

$$k_{obs.}[A][B] = \text{rate} = k_2\,[AS][B] = k_2K[S][A][B]$$

Hence $$k_{obs.} = k_2K[S]$$

and $$E_A = E_2 - Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Taking the true value of the activation energy E_2 as that given by equation (4), we have thus a means of calculating Q from kinetic measurements. Hundreds of examples have been investigated, and it is a simple matter to calculate Q in each case. Unfortunately, however, the corresponding values of Q determined independently from non-kinetic data do not appear to exist in any single instance, so we can only illustrate our ideas in a general way. Combining equations (3) and (5), we have

$$E_2 - E_A = 2\mu_A\mu_B/Dr_0^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Substituting into equation (4), we have

$$k = \sigma_{1,2}^2\{8\pi kT(1/m_1 + 1/m_2)\}^{\frac{1}{2}} \,.\, e^{-(E_A + 2N_0\mu_A\mu_B/Dr_0^3)/RT} \quad . \quad . \quad . \quad (7)$$

where N_0 is the Avogadro constant. We have ignored the fact that both the collision frequency and the dielectric constant vary with the temperature; since D varies exponentially with T (Lowry and Jessop, J., 1930, 782; Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125), the correction can be conveniently included. It has been omitted, partly because it is relatively small, but chiefly so as not to cloud the issue. After making as impartial a survey of the data as is possible, we conclude that, in a general way, equation (7) summarises satisfactorily the salient points revealed by the slow reactions of the Menschutkin type; *e.g.*, it explains the comparative rapidity of these reactions in solvents of high dielectric capacity, where $2\mu_A\mu_B/Dr_0^3$ is small, and the velocity approaches what has been termed the normal value, *i.e.*, that given by equation (4). It also explains the observation (Grimm, Ruf, and Wolf, *Z. physikal. Chem.*, 1931, *B*, **13**, 301) that, in solvents of similar dielectric constant (*e.g.*, the phenyl halides), the velocity increases with a decrease in the dipole moment of the solvent molecules.

The application of equation (7) to Cox's data (J., 1921, **119**, 142) on the aniline–bromoacetophenone reaction is illustrated in Table II. It will be observed, first, that the magnitude

TABLE II.

The Reaction between Aniline and Bromoacetophenone in Various Solvents.

Solvent.	E_2.	E_A.	$(E_2 - E_A)$.	D.	$\mu_S \times 10^{18}$.
C_6H_6	24,590	8,090	16,500	2·28	0·2 (C–H)
$CHCl_3$	23,970	10,760	13,210	5·05	0·95
$COMe_2$	22,210	11,080	11,130	*ca.* 20	2·75
$CH_3{\cdot}OH$	21,420	12,440	8,980	33·7	1·60
$C_2H_5{\cdot}OH$	21,440	13,910	7,530	26·8	1·60
$C_6H_5{\cdot}CH_2{\cdot}OH$	21,810	14,290	7,520	15·9	—
$C_6H_5{\cdot}NO_2$	22,500	13,470	9,030	36·1	1·9 (?)

of $(E_2 - E_A)$ lies near that of the non-kinetic quantity Q, of Table I. A more significant observation is that the expected parallelism between $(E_2 - E_A)$ and $2\mu_A\mu_S/Dr_0^3$ is maintained in solvents of low dielectric capacity (those placed above the line) and breaks down for the hydroxylic solvents and nitrobenzene. The explanation we offer is that the dipole–dipole interaction between reactant and solvent is now so great as to cause actual ionisation, *e.g.*, $C_6H_5{\cdot}NH_2 + CH_3{\cdot}OH \rightleftharpoons C_6H_5{\cdot}NH_3^{\cdot} + OH'$ (cf. $NH_3 + HOH \rightleftharpoons NH_4^{\cdot} + OH'$). In fact, the velocity of reaction in alcoholic solution approaches the value to be anticipated if one of the reactants were completely ionised, and is consistent with the idea of partial, or incipient, ionisation as described here. If the present explanation is correct, the reactions between halides and nitrogen bases are intermediate in character between reactions which are wholly non-polar and those where one of the participants is unambiguously ionic. Accepting Cox's data, and applying the admittedly approximate method of calculation described here, we obtain the following values for the critical separation of the dipoles in the intermediate complex : 0·73 Å. in benzene, 2·26 Å. in chloroform, and 3·33 Å. in nitrobenzene. The agreement is sufficiently close to enable us to conclude that these reactions, which have been usually referred to as "slow," have normal velocities, provided the correct energy of activation is used in the calculation.

New and more accurate experimental material for testing equation (7) has been provided

by Winkler and Hinshelwood (J., 1935, 1147) on the union of amines and halides in benzene solution. Of the numerous predictions of the theory, three examples of which are illustrated in Table III, only two are not in agreement with experiment. Change of the iodine atom

TABLE III.

Reaction.	E_A.	(E_2-E_A).	$\mu \times 10^{18}$.	Reaction.	E_A.	(E_2-E_A).	$\mu \times 10^{18}$.
NMe_3+MeI	8,790	11,490	1·6 (MeI)	NMe_3+MeI	8,790	11,490	0·82 (NMe_3)
NMe_3+EtI	11,400	11,520	1·7 (EtI)	NEt_3+MeI	9,300	12,700	0·90 (NEt_3)
NMe_3+Pr^{a}I	11,200	13,140	1·85 (Pr^{a}I)	C_5H_5N+Pr^{a}Br	15,900	12,150	1·97 (Pr^{a}Br)
				C_5H_5N+Pr^{a}I	16,100	10,770	1·85 (Pr^{a}I)

from the α- to the β-position should cause $(E_2 - E_A)$ to increase about 7%, whereas experiment shows it to decrease by this amount. Secondly, our elementary calculations have not succeeded in explaining the difference observed on passing from an aliphatic amine to an aromatic one. The intermolecular complex in the latter case possibly requires some other geometric arrangement, or a simple 1 : 1 complex is not formed.

Similar considerations apply to the apparently unimolecular decomposition of carboxylic acids in various solvents. The difference between the critical increment for the decarboxylation of camphorcarboxylic acid in water and in aniline is 8,700 cals. (*op. cit.*, p. 156). Accepting the value in water as the standard value, because it is nearly equal to that in the fused state, we may ascribe the catalytic effect of aniline to the exothermic formation of a molecular complex, prior to decomposition. Taking $\mu_1 = 1{\cdot}5$, $\mu_2 = 2{\cdot}5$, and $D_{NH_2Ph} = 7{\cdot}25$, we find, from $\Delta E = 2\mu_1\mu_2/Dr_0^3$, that $r_0 = 1{\cdot}20$ Å.

It is to be noted that the occurrence, rather than the velocity, of dipole–dipole interaction is the significant fact in the study of the kinetics of the formation of quaternary ammonium salts.

Reactions involving the Interaction of a Dipole and an Induced Dipole.—The term non-polar solvent is apt to be misleading, because the very existence of the liquid state implies a certain polarity; *e.g.*, carbon tetrachloride is only effectively non-polar, owing to the fact that its four live dipoles are equal and symmetrically oriented. In the presence of foreign molecules, the symmetry may be disturbed and the molecule as a whole become slightly polar. The effect is due to the superposition on the permanent dipole of an additional dipole induced by the presence of neighbouring molecules or ions. The polar inducibility of bonds in compounds which are normally non-polar is a subject of some importance in general chemistry. We propose to gather here some of the unco-ordinated facts.

The dipole moment of certain substances is greater in non-polar solvents such as heptane than in the vapour phase, indicating an influence due to the alleged non-polar solvent (Jenkins, *Trans. Faraday Soc.*, 1934, **30**, 739; Smythe and McAlpine, *J. Chem. Physics*, 1935, **3**, 320). The polarisability of bonds such as C–Cl in carbon tetrachloride and of C–H in hydrocarbons probably accounts for the fact that the union of amines and halides in these solvents is quite different from what it is in the "vapour" phase. One of the reactants has clearly induced a dipole in the solvent molecules. In their behaviour towards reactions of the Menschutkin type, solvents such as carbon tetrachloride, hexane and benzene are certainly not inert. On the other hand, solutes such as chlorine monoxide in carbon tetrachloride exhibit no such effect, and the velocity and mechanism of decomposition in the gas phase and in solution are the same.

The following interesting facts have been pointed out by Sidgwick ("The Covalent Link in Chemistry," Cornell University Press, 1933, p. 135):

Iodine in hexane is non-polar; in benzene, $\mu = 1$.
Aluminium bromide in hexane is non-polar; in benzene, $\mu = 4{\cdot}89$.

The first observation can be correlated with the solubility of iodine in various solvents: in carbon tetrachloride, it is sparingly soluble; in chloroform at room temperature it is about twice as soluble (Briner, *Z. physikal. Chem.*, 1898, **26**, 147); in methylene iodide it is very soluble, and in methane abundantly soluble. The solubility of iodine is thus

closely linked with the presence of the C–H bond in the solvent molecule and with the high polarisability of the iodine molecule. The conclusion is of interest in connection with Hinshelwood's suggestion that the catalytic action of iodine molecules in the gaseous decomposition of ethers and aldehydes (which, of course, contain C–H bonds) may be connected with the high polarisability of the catalyst. The other halogens have not such a marked catalytic effect.

The variability of the dipole of aluminium bromide is suggestive in view of the fact that this compound typifies the most effective catalyst for reactions of the Friedel–Crafts category, *e.g.*, $R{\cdot}COCl + C_6H_6 \longrightarrow R{\cdot}CO{\cdot}C_6H_5 + HCl$. Reactions of this type are also catalysed, in order of diminishing efficacy, by aluminium, antimonous, and arsenious chlorides. The compounds $C_6H_6,2SbCl_3$ and $C_6H_6,2SbBr_3$ have been isolated, and their existence is in all probability due to the interaction between the permanent dipole of the inorganic molecule and the dipole which it induces in the organic molecule. In the case of aluminium bromide in benzene solution (above), the magnitude of the dipole is so great that if it were, so to speak, concentrated in one bond, it would render ionisation in benzene solution fairly facile. In solution in nitrobenzene, which possesses greater dielectric capacity, we are therefore entitled to expect substances like aluminium bromide to exist largely in the ionic form. The absolute velocity of the reaction $Cl_2 + C_6H_5{\cdot}NO_2 \longrightarrow HCl + m\text{-}C_6H_4Cl{\cdot}NO_2$ (Goldschmidt and Larson, *Z. physikal. Chem.*, 1904, **48**, 424) catalysed by ferric, stannic, or aluminium chloride in nitrobenzene solution can be shown to be, in fact, consistent with values calculated on the basis of a termolecular mechanism involving an ion.

In a table containing much data, Hildebrand ("Solubility," Chemical Catalog Company, New York, 1924, p. 63) shows that the greatest deviation from Raoult's law occurs in the case of the mutual solubility of stannic chloride and benzene. Neither of these substances shows a resultant dipole moment alone, but in the presence of one another mutually induced dipoles determine the property to a large extent.

The existence of crystalline hydrates of methane and of the rare gases argon, krypton, and xenon (Sidgwick, "The Electronic Theory of Valency," Oxford, 1927) must be attributed to the interaction of the dipole of the water molecule and the dipole which it induces in the normally non-polar molecule or atom. The magnitude of the induced dipole depends on the polarisability of the atom in question; hence it is easy to understand why hydrates of helium and neon (which have low polarisabilities) are not known.

Reactions between an Ion and a Dipole.—The energy of attraction between an ion of charge ze and a permanent dipole μ situated at a distance r from it is

$$\varepsilon = ze\mu/Dr^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

With r in Å., and μ in Debye units, $\varepsilon = 70{\cdot}3z\mu/Dr^2$ kg.-cals./mol.

when the ion lies on the projected axis of the dipole. The most important class of compounds which owe their existence to such interactions are solvated ions.

All ions in aqueous solution exist in the hydrated form (ion, nH_2O). The electrostatic attraction is due to the ionic charge and to the permanent dipole of the water molecules, and, as will be shown, is usually fairly large. The phenomenon of solvation is not, of course, confined to water, but is a general property of all solvents the molecules of which possess permanent dipoles (non-polar solvent molecules are discussed below). The hydration of ions in solution has been investigated by a variety of methods, depending on the determination of properties such as the density, viscosity, freezing point, electrical conductivity, electrical transport, and the influence of neutral salts on solubility. In no case, however, can one decide quantitatively about the number of water molecules which are combined with a particular ion. The term n is, in fact, a statistical number. Furthermore, as equation (8) implies, each ion is attracted by all the solvent molecules in the system, to an extent depending on the separation. Some quantitative idea of the magnitude of the energy of hydration may be obtained by ascribing the electrostatic effect solely to those solvent molecules which are adjacent to the ion, and gauging their number from our knowledge of crystal structure; *e.g.*, the lattice energy of the sodium bromide crystal is 170,000 cals./

g.-mol. (J. Sherman, *loc. cit.*). The heat of dissolution of this salt at infinite dilution is practically zero, the exact value being 100 cals. (Fajans and Schwartz, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 717), hence the sum of the heats of hydration of the bromide and sodium ions must be about 170,000 cals. If we assume that this quantity is equally shared between the two ions, and further, that a shell consists of six water molecules, we have a value of about 14,000 cals. for the energy of interaction of the ion and a single dipole. In many cases, the process of dissolution is exothermic (*e.g.*, 11,700 cals. for lithium bromide and 14,800 cals. for lithium iodide in water), but it is always small compared with the lattice energy. From a consideration of similar magnitudes, Guggenheim ("Chemistry at the Centenary Meeting of the British Association," 1931, p. 58) has concluded that all monatomic ions in water are thoroughly hydrated. Because of these large heats of hydration, many reactions are rendered possible in solution, which could not occur in the gas phase. The importance of this conclusion has been demonstrated by Ogg and Polanyi (*Trans. Faraday Soc.*, 1935, **31**, 511). The profound change in the equilibrium position of certain reactions, due to the presence of a solvent, is further illustrated by the following examples :

$$\begin{cases} H_2O_2\,(\text{gas}) + I_2\,(\text{gas}) = 2HI\,(\text{gas}) + O_2\,(\text{gas});\ \Delta F^0_{298^\circ} = 19{,}470 \text{ cals.} \\ H_2O_2\,(\text{aq.}) + I_2\,(\text{aq.}) = 2H^\cdot\,(\text{aq.}) + 2I'\,(\text{aq.}) + O_2\,(\text{gas});\ \Delta F^0_{298^\circ} = 820. \end{cases}$$

$$H_2S\,(\text{gas}) + I_2\,(\text{solid}) = S\,(\text{solid}) + 2HI\,(\text{gas});\ \Delta F^0_{298^\circ} = 7{,}210.$$

$$H_2S\,(\text{aq.}) + I_2\,(\text{solid}) = S\,(\text{solid}) + 2H^\cdot\,(\text{aq.}) + 2I'\,(\text{aq.});\ \Delta F^0_{298^\circ} = -18{,}230.$$

Ions are hydrated, not only in solution, but in crystal hydrates such as $BaCl_2,H_2O$; $LaCl_3,6H_2O$, etc. In these cases, also, it is reasonable to ascribe the dominant rôle to the interaction between ions and dipoles. Table IV gives the magnitudes of the heats of hydration (cals./g.-mol.) of a few ionic crystals. Analogous compounds are $AgCl,3NH_3$; $CaCl_2,6NH_3$, etc.; and instances of compounds containing chloroform of solvation have already been cited.

TABLE IV.

Hydrate	$KF,2H_2O$	$NaBr,2H_2O$	$NaI,2H_2O$	$LiBr,2H_2O$	$BaCl_2,2H_2O$
Heat of hydration	4,600	4,520	5,230	10,050	7,000
Hydrate	$BaCl_2,H_2O$	$SrCl_2,2H_2O$	$SrCl_2,H_2O$	$MgSO_4,H_2O$	
Heat of hydration	3,170	9,060	5,260	6,980	

Reactions between an Ion and an Induced Dipole.—The moments of dipoles induced by ions are usually less than those of the permanent dipoles. Where a permanent dipole exists in the absence of an ion, the two interactions are superimposable, but an ion–induced dipole interaction may exist without a permanent dipole being present. In order to induce a moment μ, an energy $\mu^2/2\alpha$ must be expended, where α is the polarisability. The energy of combination of an ion of charge e and a dipole μ is given (see above) by $\varepsilon = e\mu/r^2$. Hence the total energy gained by the process of polarisation and attraction of the ion and the induced dipole (in a vacuum) is

$$\frac{e\mu}{r^2} - \frac{\mu^2}{2\alpha} = \frac{\alpha e^2}{r^4} - \frac{\alpha^2 e^2}{2\alpha r^4} = \frac{\alpha e^2}{2r^4} = 164{\cdot}9/r^4 \text{ kg.-cals./mol.} \quad . \quad . \quad . \quad (9)$$

for $\alpha = 1$ (r in Å.).

The Relation between the Electrostatic Attraction of Ion and Dipole and the Attraction designated as a Co-ordinate Link.—It is the object of this section to show that there is no incompatibility between the ideas of an ion–dipole bond and of the co-ordinate linkage. Let us consider the formation of the ammonium ion from a proton and a molecule of ammonia, $H^\cdot + NH_3 \longrightarrow [NH_4]^\cdot$. According to the principle outlined here, the newly-formed bond exists in virtue of the compensating effect of a repulsive force (which is dominant at small separations) and an electrostatic attractive force (dominant at great separations). The ammonium ion, however, is symmetrical; all the bonds in it are equal, and they must be covalent bonds, hence the ion–dipole bond must be a precursor of a covalent bond when the latter is formed in the presence of an ion. According to the conventional theory of valency, the formation of the ammonium ion is due to the sharing of the two lone

electrons in the ammonia molecule between this molecule and the proton. Sidgwick, to whom the term co-ordination is due, has been careful to apply it to the process of formation and has, rightly, not insisted that the bond, once formed, is in any way different from a covalent bond formed when two atoms unite. The terms "electron donation" and "ion–dipole attraction" are thus not mutually exclusive, but are alternative attempts to describe the same phenomenon. The present approach is more helpful in some respects. For example, it enables us to understand why the complex $[Cu(NH_3)_4]^{\cdot\cdot}$ exists, and why there is no such complex as $[Cu(He)_4]^{\cdot\cdot}$. On the other hand, the present view would never have led us to Sidgwick's covalency rule.

From the quantum-mechanical aspect, the state of system $[Cu(NH_3)_4]^{\cdot\cdot}$ can be represented by a wave function ψ. Supposing that it is possible for the system to exist in two states which have very nearly the same energies, the wave function of the system may be expressed approximately as a linear combination of the fnnctions ψ_a and ψ_b, thus $\psi = a\psi_a + b\psi_b$. If ψ_a denotes the ion–dipole state, and ψ_b the co-ordinate state, the two states can clearly co-exist, or the system may be entirely of one kind (*e.g.*, $a = 1$, $b = 0$) or the other ($a = 0$, $b = 1$).

Conclusion.—It has been our object to emphasise the importance of considering the variety of electrostatic attractions in dealing with systems in the condensed phase. The scheme of classification of chemical equilibria which such considerations make possible includes the difficult problems of solubility, solvation and the kinetics of reactions in solution. Each of these will ultimately require careful quantitative treatment, and we have therefore here confined ourselves to a purely descriptive outline of the principles involved. At least one of the numerous problems raised here has already been the subject of quantitative examination, *viz.*, the kinetics of ion–dipole reactions, investigated by Ogg and Polanyi (*loc. cit.*). The success which has attended their work is encouraging, and indicates the necessity of similar treatments for the numerous problems which, according to the present scheme, are outstanding. One or two of these we hope to deal with in a forthcoming publication.

Scant attention has here been paid to reactions involving only the making or breaking of covalent bonds (in the absence of ions) because, as previously stated, we believe them to reveal no features peculiar to solutions.

Summary.

If the kinetics of reaction are different in the gas phase and in solution, the solvent is responsible for the disturbance, which, in general, is electrostatic in nature.

Electrostatic attractions are of six kinds, depending on the interactions of ions, permanent dipoles, and induced dipoles, taken in pairs. The balancing of these six attractive forces by the repulsive force which characterises all interatomic systems at low separations gives rise to six types of bond, which are, however, not strictly different, though it is convenient to regard them as such. The various types of bond are severally discussed in relation to the influence of complexes on the kinetics of reactions in solution. In dealing with ionic reactions, it is pointed out that the Debye–Hückel expression refers to purely interionic attractions, whereas the so-called ionic reactions, in the kinetic study of which the expression has been so extensively applied, usually involves the interaction between an ion and a dipole as well. The interaction between two molecules, both of which possess permanent dipoles, is held responsible for the formation of several intermolecular complexes, and for the apparently slow velocity of certain bimolecular reactions in solution. The catalytic effect of substances such as aluminium chloride towards the Friedel–Crafts reaction, the existence of hydrates of methane and the rare gases, and certain solubility effects can be traced to the interaction of a permanent dipole with an induced dipole. The solvation of ions and the formation of crystalline hydrates imply an ion–permanent dipole interaction, the relation of which to the co-ordinate link is discussed.

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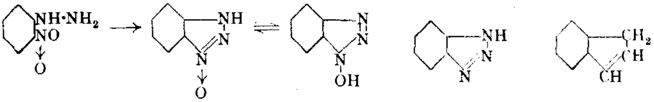
24. *The Absorption Spectra of 1 : 2 : 3-Benztriazoles.*

By A. Killen Macbeth and J. R. Price.

Hydroxy-1 : 2 : 3-benztriazoles are produced by the action of bases on *o*-nitrophenylhydrazines, the yield depending on experimental conditions (Macbeth and Price, J., 1934, 1637). Since evidence has been submitted that the nitrophenylhydrazines are not to be formulated as quinonoid compounds (J., 1935, 1563), the reaction indicates that the triazoles may be *N*-oxides (I) rather than the tautomeric hydroxy-forms (II). This question has been examined more fully by spectrophotometric methods, and the results of the study of the absorption spectra of a series of 1 : 2 : 3-benztriazoles and their derivatives are now recorded.



(I.) (II.) (III.) (IV.)

The analogy between 1 : 2 : 3-benztriazole (III) and indene (IV) might suggest that their spectra should be of similar types, especially since it is known from the comparison of the spectra of benzene and pyridine that the replacement of CH by N in a ring does not greatly affect the positions of the $\lambda_{max.}$ of the bands. This view is further strengthened by the observation (Morton and de Gouveia, J., 1934, 916) that quinoline, *iso*quinoline, and naphthalene show the same three main regions of absorption, but with intensity differences. There is no evidence, however, that electronic excitation in the azo-group will give rise to a band similar to that of the ethenoid system. Indeed, the data available indicate that the electron of the $N\overset{*}{=}N$ group gives rise to two bands; for a qualitative examination by Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3011) shows that diazoacetic ester has two maxima of absorption, one of low and the other of high persistence, at *ca.* 370 and 244 mμ respectively. Azomethane, NMe:NMe, which is a better substance for comparison on account of its more definite structure, gives a band at *ca.* 350 mμ and a marked inflexion at *ca.* 245 mμ. The introduction of a benzene ring causes changes in the intensities of the bands and displacement towards longer wave-lengths, benzeneazomethane, NPh:NMe, showing two bands at 400 and 260 mμ approximately (Stobbe and Nowak, *Ber.*, 1914, **47**, 578). The latter region expresses the absorption of the benzenoid centre and masks the second maximum of the $N\overset{*}{=}N$ group, but the shape of the curve suggests that it may be capable of resolution by the more exact methods of spectrophotometry. Benzeneazoethane gives practically identical absorption, and the line of the curves indicates the existence of a third band, characteristic of $\overset{*}{Ph}{\cdot}N{=}N{-}$, just beyond the region examined. The introduction of a second benzene ring conjugated to the azo-linking causes further displacement of the maxima to 436 mμ (log ε = 2·84) and 318 mμ (log ε = 4·37), together with a significant inflexion at 300 mμ (log ε = 4·23) and a third band due to $\overset{*}{Ph}{\cdot}N{=}N{-}$ which is clearly shown at 229 mμ (log ε = 4·09) (Macbeth and Maxwell, J., 1923, **123**, 370).

It therefore seems clear that electronic excitation of the $N\overset{*}{=}N$ group gives rise to two bands; and in order to deduce the probable absorption of the 1 : 2 : 3-benztriazoles it is further necessary to consider the effect of the third nitrogen atom and of ring closure. Some idea of the first effect may be gained by comparing the spectra of benzeneazomethane and tolueneazodimethylamine, $C_6H_4Me{\cdot}N{:}N{\cdot}NMe_2$; and the curves of azobenzene and diazoaminobenzene furnish a second comparison pair. Qualitative records only are available in all the cases apart from azobenzene (Hantzsch and Lifschitz, *loc. cit.*), and too great reliance cannot therefore be placed on the maxima recorded. From the values summarised below, however, it is seen that the introduction of the third nitrogen atom results in the

disappearance of the band of longer wave-length associated with the $\overset{*}{N}{=}N$ system, its position being marked by an inflexion which in the case of tolueneazodimethylamine is of a very minor character indeed. The shape of the qualitative curve again suggests that the band at *ca.* 280 mμ in this compound may be capable of resolution by spectrophotometric methods.

Azomethane		245		*350* ↓				
Benzeneazomethane	*	260 ↙ ↘		400 ↓	→ Tolueneazodimethylamine	*	280	*370* †
Azobenzene	*229*	*300*	318	436	→ Diazoaminobenzene	*	345	*440* †

* Band indicated outside the region of the qualitative curves. † Weak inflexion.

Ramart-Lucas and Amagat (*Bull. Soc. chim.*, **1932**, **51**, 965) have shown, from the study of allylbenzene and a series of compounds of the type $Ph{\cdot}[CH_2]_n{\cdot}CH{:}CH_2$, that a double bond which is not conjugated to the benzene ring has no influence on the benzenoid absorption; and it may therefore be inferred that ring closure which does not bring conjugation of this type into play will not materially affect the locations or intensities of the maxima characteristic of electronic excitation of the C=C system of the nucleus. This view is supported by the facts (i) that the spectra of the above compounds resemble those of ethylbenzene, the xylenes, and hydrindene; and (ii) that the styrene series, $CHPh{:}CH{\cdot}[CH_2]_n{\cdot}CH_3$, also examined by Ramart-Lucas and Amagat (*loc. cit.*), give maxima closely related to those of indene (Morton and de Gouveia, J., **1934**, 911). In the case of the triazoles, however, ring closure introduces a nitrogen atom as a substituent in the benzene ring, and this effect must not be overlooked. The introduction of the amino-group causes marked displacement of the benzene bands; *e.g.*, in aniline, the 254 mμ maximum of benzene is displaced to 284·5 mμ with increased intensity, and the short-wave band at 190 mμ is brought within the region ordinarily explored and located at 234 mμ. On the other hand, the hydrochlorides and acetyl derivatives of the bases do not show this displacement. Since the triazoles are not markedly basic, the introduction of the nitrogen atom into the nucleus may be more rightly regarded as parallel to the substituent in the acyl derivatives of the bases rather than as analogous to the substitution of the basic amino-group. On this view, the spectra of the triazoles should be similar to that of tolueneazodimethylamine, and we may therefore look for a maximum characteristic of the $\overset{*}{P}h{\cdot}N{:}N{\cdot}$ system, together with a band due to the electron of the azo-group influenced by the nucleus, $Ph{\cdot}\overset{*}{N}{=}N$, and possibly a weak inflexion also due to electronic excitation of the azo-group. The maxima found in the compounds examined are shown in Table I, italicised figures in all tables representing inflexions (see Fig. 1).

TABLE I.

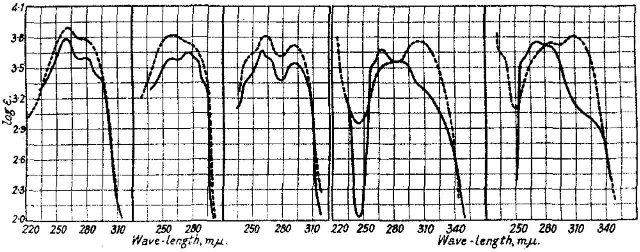
	In alcohol. $\lambda_{max.}$, mμ.	log ε.	Absorbing centre.*	In water. $\lambda_{max.}$, mμ.	log ε.	Absorbing centre.*
1 : 2 : 3-Benztriazole	*291*	3·32				
	282·5	3·58	*b*	*275·5*	3·75	*b*
	276	3·65		260·5	3·82	*a*
	259	3·58	*a*			
1-Methyl-1 : 2 : 3-benztriazole	*291·5*	3·45	*b*	*277*	3·77	*b*
	279·5	3·59		261	3·88	*a*
	258·5	3·79	*a*			
3 : 6-Dimethyl-1 : 2 : 3-benztriazole	292·5	3·55	*b*	291	3·73	*b*
	263	3·61		262	3·82	*a*
	258·5	3·68	*a*	*247*	3·65	
	244·5	3·40				

* $a = \overset{*}{P}h{\cdot}N{=}N{\cdot}N{\cdot}$; $b = Ph{\cdot}\overset{*}{N}{=}N{\cdot}N{\cdot}$.

It will be seen that the absorption of the 1 : 2 : 3-triazoles is separable into two regions *viz.*, 245—263 mμ and 270—291 mμ, the spectra in alcohol being better defined than those in water, in which an envelope of somewhat greater intensity is formed in all cases. Sub-

stitution of methyl groups leads to better resolution and clearer definition of the regions, an effect which is paralleled, *e.g.*, in the middle regions of absorption of the alkylnaphthalenes (Morton and de Gouveia, *loc. cit.*) and in the dinitrophenyl- and dinitrotolyl-hydrazines (J., 1935, 1563). From the comparative study of the qualitative curves of azomethane, benzeneazomethane, etc., discussed above, it seems reasonable to attribute the band of shorter wave-length to the C=C system of the nucleus influenced by N=N. On this view the 254 mμ band of benzene shows but little displacement in the benztriazoles, and the benzene band of shorter wave-length still remains outside the region examined. The existence of such a band is definitely indicated by the shape of the curves of many of the triazole derivatives, notably the hydroxy-triazoles, in which the displacements of the benzene bands are of a higher order. The maxima of the triazoles are therefore not comparable with those of indene, in which both the benzene bands suffer considerable

FIG. 1. FIG. 2.



(a) (b) (c) (a) (b)

FIG. 1.—(a) 1-*Methyl*-1 : 2 : 3-*benztriazole*.
(b) 1 : 2 : 3-*Benztriazole*.
(c) 3 : 6-*Dimethyl*-1 : 2 : 3-*benztriazole*.

FIG. 2.—(a) 1-*Hydroxy*-1 : 2 : 3-*benztriazole*.
(b) 1-*Hydroxy*-6-*methyl*-1 : 2 : 3-*benztriazole*.

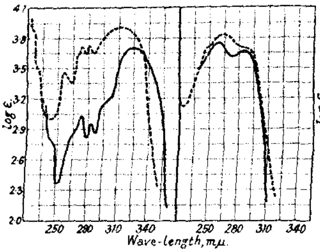
——— *in* EtOH. - - - - - *in* H_2O.

displacement under the influence of the ethenoid grouping. Morton and de Gouveia attribute the maximum at 246 mμ (log ε = 4·0) to the $Ph\cdot\overset{*}{C}{=}C$— system, and that in the region 270—290 mμ (log ε = 2·2—3·2) to $\overset{*}{Ph}\cdot C{=}C$—. The former band appears to be composite, showing in hexane a significant inflexion at 262 mμ (log ε = 3·85); the maxima at 246 and 262 mμ would thus represent respectively the displaced benzene 190 mμ band and the influenced ethenoid absorption. On the other hand, it is only the 254 mμ benzene band, but of increased intensity, which is shown in the spectra of the triazoles in association with that due to the influenced azo-group.

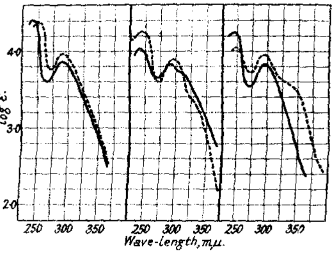
1-*Hydroxy*-1 : 2 : 3-*benztriazole*.—The absorption of this compound differs markedly in alcoholic and in aqueous solution, whereas the spectra of all the nitro-1-hydroxybenztriazoles examined closely resemble one another in both solvents. This suggests that the tautomerism between the forms (I) and (II) manifests itself in alcoholic solutions, but that only one form is stable in aqueous solution and in the case of the nitro-compounds. In this connexion it seems significant that methylation of 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole and its 5-methyl-compound by methyl iodide and sodium ethoxide yields only the corresponding methoxy-derivatives (Brady and Day, J., 1923, 123, 2258), whereas the 1-hydroxy-compound when methylated under similar conditions yields a mixture of the derivatives of (I) and (II) (Brady and Reynolds, J., 1928, 193). Methylation of 6-nitro-1-hydroxy-5-methyl-1 : 2 : 3-benztriazole with sodium hydroxide and methyl sulphate, however, yields a little of the *N*-oxide derivative as a secondary product (Brady and Day, *loc. cit.*).

Definite evidence in favour of the existence of the two tautomeric forms (I) and (II) in alcoholic solution is found on examination of the curves of their methyl derivatives and analysis of the absorption of the substance itself in alcoholic solution. The graphs of these substances are shown in Figs. 2 and 3, and the values of the maxima are recorded

FIG. 3. FIG. 4.



(a) (b)



(a) (b) (c)

FIG. 3.—(a) 3-*Methyl*-1 : 2 : 3-*benztriazole* 1-*oxide*. —— *in* EtOH. - - - - - *in* H_2O.
(b) 1-*Methoxy*-1 : 2 : 3-*benztriazole*. —— *in* EtOH. - - - - - *in* H_2O–MeOH.

FIG. 4.—(a) ——— 6-*Nitro*-1 : 2 : 3-*benztriazole in* EtOH.
- - - - - 6-*Nitro*-1-*methyl*-1 : 2 : 3-*benztriazole in* EtOH.
(b) ——— 6-*Nitro*-1 : 2 : 3-*benztriazole in aqueous* EtOH.
- - - - - 6-*Nitro*-3-*methyl*-1 : 2 : 3-*benztriazole in aqueous* MeOH.
(c) ——— 6-*Nitro*-3-*methyl*-1 : 2 : 3-*benztriazole in* EtOH.
- - - - - 6-*Nitro*-1-*methyl*-1 : 2 : 3-*benztriazole in aqueous* MeOH.

in Table II. The *O*-ether shows the same regions of absorption in both alcoholic and aqueous solution, but in the latter solvent the intensities are somewhat increased. Similar cousiderations hold for the *N*-oxide.

TABLE II.

1-*Hydroxy*-1 : 2 : 3-*benztriazole*.				1-*Hydroxy*-6-*methyl*-1 : 2 : 3-*benztriazole*.			
Alcohol.		Water.		Alcohol.		Water.	
$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.	$\lambda_{max.}$, mμ.	log ε.
305—330	2·88—3·32	305	3·79	*310—330*	2·94—3·16	306	3·82
287·5	3·58	*278*	3·57	*282·5*	3·73	284	3·75
267·5	3·7			*271·5*	3·77	*234·5*	3·64
259·5	3·57			*258·5*	3·6		
3-*Methyl*-1 : 2 : 3-*benztriazole* 1-*oxide*.				1-*Methoxy*-1 : 2 : 3-*benztriazole*.			
324·5	3·73	310·5	3·92	284	3·66	*279·5*	3·74
298·5	3·17			260	3·77	262	3·83
281·5	2·96	281	3·72			*249*	3·72
273	3·04	273	3·71				
268	2·9	*268*	3·6				
242·5	2·8	257·5	3·45				
		228·5	3·5				
		223·5	3·88				

The maxima shown by the *O*-ether in alcohol are thus (*a*) 284 mμ (log ε = 3·66) and (*b*) 260 mμ (log ε = 3·77). The only maximum shown by the 3-methyl *N*-oxide of sufficient intensity to appear in combination of the two curves is (*c*) 324·5 mμ (log ε = 3·73). The corresponding locations in the hydroxybenztriazole curve are (a_1) 287·5 mμ (log ε = 3·58), (b_1) 267·5 mμ (log ε = 3·70), and (c_1) 324·5 mμ in the inflexion region 310—330 (log ε = 3·02). The difference in log ε values for (*a*) and (a_1), *viz.*, 0·08, gives 83% of (II), whilst that for (*b*) and (b_1) indicates some 85% of (II). On the other hand, (*c*) and (c_1) give a log ε difference of 0·71, corresponding to *ca.* 20% of (I) in solution. The good agreement between the values calculated for the different maxima seems to prove the existence of

an equilibrium mixture of the tautomerides in alcoholic solution corresponding to some 80—85% of (II). The absorption of alcoholic solutions of 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole presents the same features as that of the unsubstituted compound, and it therefore appears that in this case also there is an equilibrium mixture of the two forms. Calculation of the percentages is not practicable, as the curves for the corresponding methyl-substituted methoxy-derivative and 1-oxide are not available.

Nitro-derivatives of 1 : 2 : 3-*Benztriazoles.*—The spectra of 6-nitro-1 : 2 : 3-benztriazole and its 1- and 3-methyl derivatives in alcoholic solution are practically identical, absorption occurring as two well-defined bands in the regions characteristic of the alkylbenztriazoles with but little displacement. The two maxima are therefore to be attributed to the absorbing centres already specified in the case of the simple triazoles. When, however, the nitro-triazoles are examined in aqueous solution, a new inflexion is observed at *ca.* 312—330 mμ. In view of the evidence obtained from the nitro-amines (Morton and

FIG. 5. FIG. 6.

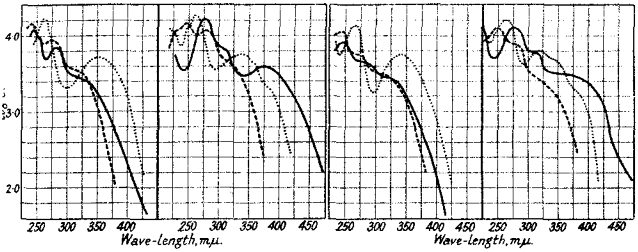


FIG. 5.—(a) ——— 6-*Nitro-1-hydroxy-*1 : 2 : 3-*benztriazole in* EtOH.
— — — 6-*Nitro-1-methoxy-*1 : 2 : 3-*benztriazole in* EtOH.
- - - - - 6-*Nitro-3-methyl-*1 : 2 : 3-*benztriazole* 1-*oxide in* EtOH.
(b) ——— 6-*Nitro-1-hydroxy-*1 : 2 : 3-*benztriazole in* H_2O.
— — — 6-*Nitro-1-methoxy-*1 : 2 : 3-*benztriazole in aqueous* MeOH (10% MeOH).
- - - - - 6-*Nitro-3-methyl-*1 : 2 : 3-*benztriazole* 1-*oxide in* H_2O.

FIG. 6.—(a) ——— 6-*Nitro-1-hydroxy-5-methyl-*1 : 2 : 3-*benztriazole in* EtOH.
— — — 6-*Nitro-1-methoxy-5-methyl-*1 : 2 : 3-*benztriazole in* EtOH.
- - - - - 6-*Nitro-3* : 5-*dimethyl-*1 : 2 : 3-*benztriazole* 1-*oxide in* EtOH.
(b) ——— 6-*Nitro-1-hydroxy-5-methyl-*1 : 2 : 3-*benztriazole in* H_2O.
— — — 6-*Nitro-1-methoxy-5-methyl-*1 : 2 : 3-*benztriazole in aqueous* EtOH (10% EtOH).
- - - - - 6-*Nitro-3* : 5-*dimethyl-*1 : 2 : 3-*benztriazole* 1-*oxide in* H_2O.

cGookin, *loc. cit.*) and the nitro- and dinitro-phenylhydrazines (Macbeth and Price, *loc.* .), it seems reasonable to attribute this region of absorption to an electron jointly con-olled by a nitrogen and an oxygen atom of the nitro-group.

The spectra of 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole and its 5-methyl derivative ive also been examined; in alcoholic solution they give curves almost identical with those the corresponding methoxy-compounds. These compounds also absorb in the two gions characteristic of the centres denoted in Table I, but show in addition the inflexion signed above to the nitro-group. The absence of any such inflexion in the alcoholic lutions of the nitrotriazoles other than the hydroxy-derivatives and their ethers con-itutes a difficulty as yet unexplained.

The curves of the nitro-derivatives of 1 : 2 : 3-benztriazole are shown in Figs. 4, 5, and 6, id the values are set out in Table III; where inflexions occur, the approximate wave-igth of the middle region is recorded. For the hydroxytriazoles the solvent was water, it with the other substances it was found necessary on account of solubility to use aqueous cohol (10% MeOH or EtOH).

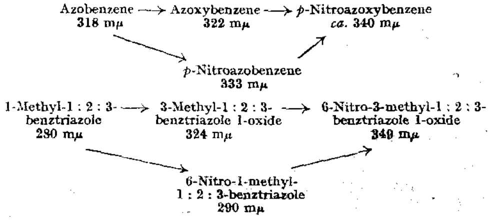
TABLE III.

Derivatives of 1 : 2 : 3-*Benztriazole.*

Solvent.	Absorbing centre.*	6-Nitro-. $\lambda_{max.}$, mμ.	log ϵ.	6-Nitro-1-methyl-. $\lambda_{max.}$, mμ.	log ϵ.	6-Nitro-3-methyl-. $\lambda_{max.}$, mμ.	log ϵ.
Alcohol	*b*	290	3·86	290·5	3·98	295	3·82
	a	240·5	4·22	250	4·21	244·5	4·26
Water	NO_2	*ca. 312*	3·7	*ca. 327*	3·63	*ca. 328*	3·37
	b	292·5	3·83	294	3·95	297	3·9
	a	241	4·05	250·5	4·05	247	4·26
		1-Methoxy-.		6-Nitro-1-methoxy-.		6-Nitro-1-hydroxy-.	
Alcohol	NO_2	—	—	*ca. 315*	3·57	*ca. 315*	3·48
	b	284	3·66	273	3·96	281	3·88
	a	260	3·77	241·5	4·16	{*254* / 247	4·01 / 4·12
Water	NO_2	—	—	*ca. 315*	3·65	375	3·59
	b	*279·5*	3·74	280	4·09	*ca. 306*	3·84
	a	{262 / *249*	3·83 / 3·72	{244 / *232*	4·17 / 4·09	274·5	4·2
		6-Nitro-1-methoxy-5-methyl-.		6-Nitro-1-hydroxy-5-methyl-.			
Alcohol	NO_2	*ca. 312*	3·5	*ca. 320*	3·45		
	b	*ca. 272*	3·75	*ca. 278*	3·66		
	a	245	4·05	249	3·92		
Water	NO_2	*ca. 320*	3·42	*ca. 375*	3·48		
	b	*ca. 274*	3·89	*ca. 312*	3·75		
	a	249	4·08	274·5	4·11		

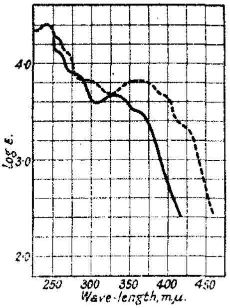
* See Table I.

1 : 2 : 3-*Benztriazole* 1-*Oxides*.—Three substances of this type, *viz.*, 3-methyl-, 6-nitro-3-methyl-, and 6-nitro-3 : 5-dimethyl-1 : 2 : 3-benztriazole 1-oxides, were examined in both aqueous and alcoholic solution. The maxima for them are recorded below and the curves are shown in Figs. 3, 5, and 6. Since these compounds differ from the benztriazoles in having a co-ordinately linked oxygen atom attached to one of the nitrogen atoms of the N=N group, some modification of the absorption characteristic of the latter is to be expected, just as a difference is observed in the case of the azo- and azoxy-compounds. Comparison of the absorption spectra of a series of azoxybenzene derivatives with that of azobenzene shows that the change from —N=N— to $\underset{\mathrm{O}}{\overset{\text{—N=N—}}{\downarrow}}$ results in a displacement of the main band (318 mμ) to longer wave-lengths, this displacement being increased by the presence of nitro-groups (Szegö, *Ber.*, 1928, **61**, 2087; 1929, **62**, 736). The diagram below illustrates the analogous behaviour of the triazole oxides, which supports the interpretation put forward concerning the location of the chromophores responsible for the absorption of the 1 : 2 : 3-benztriazoles.



The spectra of the nitro-compounds in alcoholic solution are comparatively simple, showing two well-defined maxima at *ca.* 263—265 and 340—349 mμ. As in the case of the simple 1 : 2 : 3-benztriazoles, the former is attributed to the aromatic C=C system, and the latter to the azoxy-group. In aqueous solution the two main maxima are still observed with some displacement of the second maximum towards shorter wave-lengths, and a new inflexion appears at *ca.* 379 mμ, which, by analogy with the nitro-triazoles, may be attributed to the nitro-group.

FIG. 7.



5-Nitro-3-hydroxy-αβ-naphtha-1 : 2 : 3-triazole. —— *in* EtOH. - - - *in* H_2O.

The absorption of 3-methyl-1 : 2 : 3-benztriazole 1-oxide is more complex. In addition to the main band at 324·5 mμ, which shows displacement towards shorter wave-lengths on change of solvent from alcohol to water, as with the nitro-triazole oxides, the absorption curves show a group of maxima in the region 260—280 mμ which may be attributed to the chromophore

$$\overset{*}{\text{Ph}}\text{—N=N}\underset{\text{O}}{\downarrow}$$

. The resolution in this region is more marked than with the nitro-compounds, and although increased intensity is observed on change of solvent from alcohol to water, even in the latter solvent the log ε values are much less than those found for the nitro-derivatives. The shape of the curves in both solvents gives a clear indication of another more intense maximum outside the region of examination, which probably represents the second band of benzene which has been recorded at 190 mμ.

1 : 2 : 3-*Benztriazole* 1-*Oxides.*

Solvent.	Absorbing centre.*	3-Methyl-. $\lambda_{max.}$, mμ.	3-Methyl-. log ε.	6-Nitro-3-methyl-. $\lambda_{max.}$, mμ.	6-Nitro-3-methyl-. log ε.	6-Nitro-3 : 5-dimethyl-. $\lambda_{max.}$, mμ.	6-Nitro-3 : 5-dimethyl-. log ε.
Alcohol	*c*	324·5	3·73	349	3·75	341·5	3·76
		298·5	3·17				
	d	281·5	2·96				
		273	3·04				
		268	2·90	263	4·24	265·5	4·15
		242·5	2·80				
Water	NO_2	—	—	*379*	3·34	*379*	3·28
	c	319·5	3·92	*357*	3·67	*339*	3·71
				338	3·78	318·5	3·80
	d	281	3·72				
		273	3·71				
		268	3·60	262	4·27	263	4·20
		257·5	3·45	*252*	4·17	*247·5*	4·04
		228·5	3·50				
		223·5	3·88				

* *c* = $\text{Ph·}\overset{*}{\text{N}}\underset{\text{O}}{\downarrow}\text{=N-}$; *d* = $\overset{*}{\text{Ph}}\text{·N}\underset{\text{O}}{\downarrow}\text{=N-}$.

Displacements.—The displacements on change of solvent of the maxima of some of the triazoles and their derivatives are set out below, from which it will be seen that the Δ $cm.^{-1}$ values for the nitro-hydroxy-derivatives are markedly greater than in the case of any other compound examined. This also holds for a nitro-hydroxy-naphthatriazole which was prepared and examined (Fig. 7), and is apparently connected with the ionisation of these substances in aqueous solution. The values of the simple hydroxy-derivatives of triazoles are not discussed in this connexion on account of the tautomerism already described.

Displacements : Alcohol ⟶ Water.

1 : 2 : 3-Benztriazoles.	$\lambda_{max.}$, mμ.	cm.$^{-1}$. ⟶	$\lambda_{max.}$, mμ.	cm.$^{-1}$.	Δ cm.$^{-1}$.
6-Nitro-	290	34,500	292·5	34,200	− 300
	240·5	41,600	241	41,500	− 100
6-Nitro-1-methyl-	290·5	34,400	294	34,000	− 200
	250	40,000	250·5	39,900	− 100
6-Nitro-3-methyl-	295	33,900	297	33,700	− 200
	244·5	40,900	247	40,500	− 400
1-Methoxy-	284	35,200	279·5	35,800	+ 600
	260	38,450	262	38,200	− 250
6-Nitro-1-methoxy-	273	36,600	280	35,700	− 900
	241·5	41,400	244	41,000	− 400
6-Nitro-1-methoxy-5-methyl-	312	32,050	320	31,250	− 800
	272	36,750	276	36,250	− 500
	245	40,800	249	40,200	− 600
6-Nitro-1-hydroxy-	*ca.* 315	31,750	*ca.* 375	26,650	− 5100
	281	35,600	306	32,700	− 2900
	247	40,500	274·5	36,400	− 4100
6-Nitro-1-hydroxy-5-methyl-	*ca.* 320	31,250	*ca.* 375	26,650	− 4600
	278	36,000	312	32,050	− 3950
	249	40,200	274·5	36,400	− 3800
5-Nitro-3-hydroxy-αβ-naphtha-	360	27,800	398·5	25,100	− 2700
	333	30,000	363·5	27,500	− 2500
	274	36,500	294	34,000	− 2500
	255	39,200	269	37,200	− 2000

Experimental.

6-Nitro-1-hydroxy-5-methyl-1 : 2 : 3-*benztriazole* was obtained in excellent yield by refluxing 4 : 6-dinitro-*m*-tolylhydrazine on a water-bath with alcoholic ammonia until the solution became quite clear (*ca.* 5 hours) ; it was precipitated by addition of dilute hydrochloric acid after removal of the alcohol, and several crystallisations from dilute alcohol afforded pale yellow prisms, m. p. 196—197° (Brady and Day, *loc. cit.*, give 194°).

1-*Hydroxy*-6-*methyl*-1 : 2 : 3-*benztriazole*.—*p*-Chlorotoluene (100 g.) nitrated with nitric acid (*d* 1·42 ; 120 g.) and concentrated sulphuric acid (170 g.) gives a mixture of 2- and 3-nitro-4-chlorotoluene. The fraction, b. p. 255—260°, is rich in 3-nitro-4-chlorotoluene ; this (5 g.) was refluxed for 20 hours with excess of an aqueous-alcoholic solution of hydrazine hydrate, the unchanged material removed with ether, and the solution acidified with hydrochloric acid. The required *compound* was precipitated, and crystallised from dilute alcohol as colourless needles, m. p. 178—179° (Found : N, 28·3. $C_7H_7ON_3$ requires N, 28·2%).

5-*Nitro*-3-*hydroxy*-αβ-*naphtha*-1 : 2 : 3-*triazole*.—2 : 4-Dinitrochloronaphthalene (25 g. ; Ullmann and Bruck, *Ber.*, 1908, **41**, 3932) was heated on a water-bath for 6 hours with alcohol (180 c.c.) and 50% hydrazine hydrate (20 c.c.), and the mixture filtered hot. The residue was extracted with boiling water, and on cooling the hydrazine salt of 2 : 4-dinitro-α-naphthol separated. This was removed, and acidification of the solution with dilute hydrochloric acid afforded the triazole as a flocculent precipitate which, after several crystallisations from alcohol, detonated at 236° (Muller and Weisbrod, *J. pr. Chem.*, 1925, **111**, 307, give 215°). Other triazoles used in the work were prepared by standard methods. 6-Nitro-3 : 5-dimethyl-1 : 2 : 3-benztriazole 1-oxide, recrystallised successively from water (twice), methyl alcohol, and benzene, had m. p. 268—269° (Brady and Day, *loc. cit.*, give m. p. 265°) ; 6-nitro-1-methoxy-1 : 2 : 3-benztriazole, m. p. 130° ; 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole detonates at 206° ; 6-nitro-1-methoxy-5-methyl-1 : 2 : 3-benztriazole, m. p. 134—135° (Brady and Day, *loc. cit.*) ; 6-nitro-1-methyl-1 : 2 : 3-benztriazole, colourless needles, m. p. 188° (Brady and Reynolds, J., 1930, 2672, reported pale yellow needles, m. p. 187°) ; 6-nitro-3-methyl-1 : 2 : 3-benztriazole, m. p. 197—198°, and its 1-oxide, m. p. 163° (Brady and Reynolds, J., 1931, 1277) ; 1-methoxy-1 : 2 : 3-benztriazole, m. p. 88—89° ; 3 : 6-dimethyl-1 : 2 : 3-benztriazole, m. p. 49° ; 3-methyl-1 : 2 : 3-benztriazole 1-oxide, m. p. 144—145° (Brady and Reynolds, J., 1928, 198) ; 1 : 2 : 3-benztriazole, m. p. 97—98° (Ladenburg, *Ber.*, 1876, **9**, 222) ; 1-methyl-1 : 2 : 3-benztriazole, m. p. 64—65° (Reissert, *Ber.*, 1914, **47**, 676) ; 6-nitro-1 : 2 : 3-benztriazole, m. p. 211° (Zincke, *Annalen*, 1900, **311**, 290).

Summary.

(1) 1 : 2 : 3-Benztriazole and its derivatives absorb in two main regions, the shorter-wave region being attributed to an electron in the C═C system of the benzene nucleus,

and the other being assigned to the N=N of the triazole ring. The introduction of alkyl substituents into the nucleus results in improved separation of the two regions.

(2) For the nitro-compounds no absorption characteristic of this group is observed unless (*a*) an aqueous solvent is used, or (*b*) a methoxyl or hydroxyl group is present in the triazole ring.

(3) 1-Hydroxy-1 : 2 : 3-benztriazole exists in alcoholic solution as an equilibrium mixture of the two tautomeric forms, some 20% of the 1-oxide being present. Similar behaviour is also observed in the case of 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole. The nitro-hydroxy-triazoles exist as the stable hydroxy-form in both alcoholic and aqueous solution.

(4) Marked displacements of the maxima are found on change of solvent from alcohol to water in the case of the nitro-hydroxytriazoles, a behaviour which is probably connected with the ionisation of the compounds in the latter medium.

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25. *Adsorption at the Interface between Two Fluids. Part I. The Adsorption of Methylene-blue, Methyl-orange, Congo-red, and Orange-II at Benzene–Water and Chlorobenzene–Water Interfaces.*

By C. W. GIBBY and C. C. ADDISON.

VERY few quantitative investigations of adsorption at liquid–liquid interfaces are on record. Lewis (*Phil. Mag.*, 1908, **15**, 499; 1909, **17**, 466) investigated the adsorption of a number of substances at the interfaces between their solutions and a hydrocarbon oil. In general, however, he records only one measurement for each substance, so that the magnitude of the experimental error is uncertain; moreover, a comparison of experimental results with Willard Gibbs's adsorption equation requires data over a considerable range of concentration. Patrick (*Z. physikal. Chem.*, 1914, **86**, 545) found the weights of various substances removed from solutions of various concentrations by a shower of small drops of mercury; only comparative results were obtained, no attempt being made to determine the area of the mercury surface, or to prove that it was saturated. Nonaka (*J. Soc. Chem. Ind. Japan*, 1928, **31**, 297) investigated the adsorption of soap at benzene–water and toluene–water interfaces, and suggested that the adsorbed layer is unimicellular.

We have measured (i) the adsorptions of four dyes from various concentrations of each in water, at water–benzene and water–chlorobenzene interfaces, near 17°; (ii) the interfacial tensions of the systems. The four dyes mentioned in the title were specially purified. Benzene and chlorobenzene were chosen because of their ease of purification, the difference in their polar natnre, and the insolubility of the dyes in them: Congo-red, methylene-blue, and methyl-orange were extremely insoluble; but orange-II dissolved very slightly when the solvents were in contact with concentrated solutions of it, but insufficiently to affect the results. The structures of these dyes, drawn to scale from data by Sidgwick and Bowen (*Ann. Reports*, 1931, **28**, 402), are shown in Fig. 1.

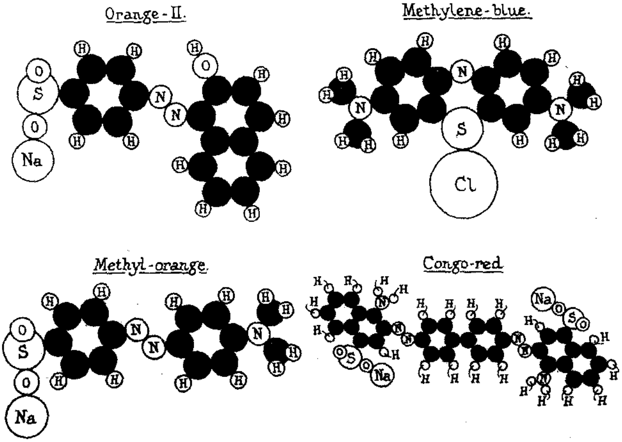
The equation first deduced by Gibbs ("Scientific Papers," I, 235), *viz.*, $\Gamma_{2,1} = -d\sigma/d\mu_2$, in which Γ is the surface excess of solute, σ the interfacial tension, and μ_2 the potential of the adsorbed component, leads to the expression $\Gamma = -c(d\sigma/dc)/RT$ in so far as the activity of the solute may be equated to its concentration (c). The quantity Γ, which must have the same dimensions as $c(d\sigma/dc)/RT$, *viz.*, those of mass per unit area, does not represent a concentration excess over that of the homogeneous part of the solution outside the range of surface forces, but the mass actually attached to unit area of the interface. The volume in which this adsorbed mass is contained is immaterial, for the surface layer was implied by Gibbs to extend to a thickness great enough to include all such adsorbed matter.

It is particularly to be observed that Gibbs's equation in this form is intended to apply only to the adsorption of a single component from a solution in which its behaviour is

ideal with reference to concentration, and that in this, or in its original form, it applies only to interfaces unaffected by electrical charges. Any deviations, therefore, of the actual equilibria from those predicted by the equation will be due to interference with one or all of these conditions.

There is already evidence that one at least of our dyes does not behave as an ideal solute in pure water, even in the low concentrations in which it is used. This evidence is only indirect, as it refers to solutions containing excess of sodium chloride and at a few concentrations of dyestuff: whereas Valkó (Faraday Society Discussion on Colloidal Electrolytes, 1935, p. 230) found orange-II to be only very slightly aggregated, with a factor of 1·2, yet for Congo-red the factor found by him was 12, by Robinson 8·6 (*ibid.*, p. 245), and by Quesnel about 12 (*ibid.*, p. 259). Concerning the molecular state of the other two solutes, we know of no experimental evidence except that of Robinson (*loc. cit.*), who finds methylene-blue to be only slightly aggregated.

FIG. 1.



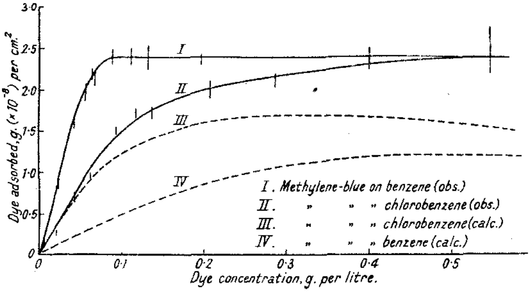
As to the second disturbing factor, since all the solutes are electrolytes in which either the cation (methylene-blue) or the anion (the others) is complex, an electrical double layer is certain to be formed at the interface with benzene or chlorobenzene. It is permissible to doubt whether the interfacial adsorption in a polar liquid like water is ever free from the formation of electrical double layers. This factor cannot, as far as we are aware, be excluded from any practicable experiment. It has, *e.g.*, been shown by Alty (*Proc. Roy. Soc.*, 1924, **106**, 315) that bubbles of air passing through the purest obtainable water were sufficiently charged to move in an electric field. He noted that two bubbles of air repelled one another; we have observed similar phenomena with drops of benzene and of chlorobenzene passing through solutions of the dyestuffs.

Accordingly, it is not surprising that our results, which we have been able to make reproducible and regular, show marked quantitative deviations from the predictions of Gibbs's equation in each of the eight cases. No reconciliation can be made by expressing the solute concentrations in terms of a polymeric molecule, or by the assumption that only a fraction of the dye is available for adsorption, whether this fraction be constant or varying in accordance with the law of mass action, or whether single molecules or the

aggregates constitute the available fraction. The equation gives values of approximately the right order of magnitude, and is in much closer agreement with our results than with Lewis's data, but there can be no doubt as to the influence of the factors referred to above.

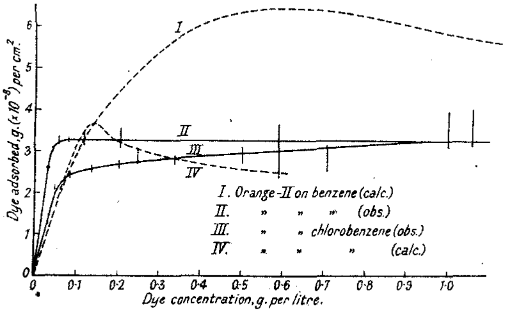
Two distinct types of concentration–adsorption curve are found here. The type differs according to the absorbate, but is independent of whether the interface is water–benzene or water–chlorobenzene.

FIG. 2.



In Type I, shown by methylene-blue and orange-II (see Figs. 2 and 3, and Table II, A, B, C, D), the curve rises fairly steeply to a maximum adsorption, and remains there even to the highest concentrations which we have been able to use. In Type II, shown by Congo-red and methyl-orange (see Figs. 4 and 5, and Table II, E, F, G, H), an initial rise to a sharp maximum is quickly followed by a fall towards, and even as far as, zero adsorption. Moreover, the numerical value of the adsorption reached in each of the

FIG. 3.



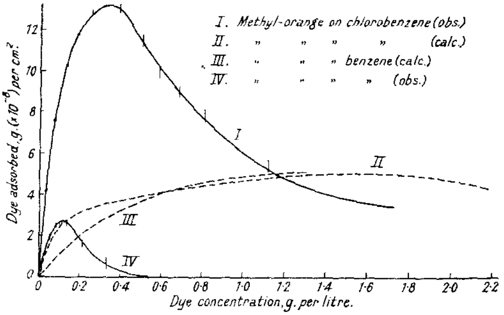
first two cases is the same, whether benzene or chlorobenzene is used; in the last two cases, chlorobenzene is a much stronger adsorbent than benzene.

Having regard to the interfacial tensions concerned, Type II has the qualitative features of a Gibbs's curve; Type I has not. The form of an adsorption curve calculated from Gibbs's equation depends, of course, upon the manner in which the interfacial tension varies with the concentration. In the cases we have studied, as the concentration in-

creases from zero, $d\sigma/dc$, which is large at low concentrations, either finally approaches zero asymptotically or diminishes rapidly. Consequently Γ passes through a maximum and approaches zero again in spite of increasing concentration.

The shapes of the experimental curves for Congo-red and methyl-orange, although similar to those required by Gibbs's equation, could equally well be accounted for qualitatively on the assumption that only single molecules are adsorbed. Two opposing

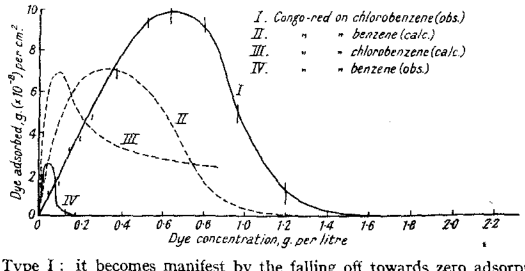
FIG. 4.



factors are then operating simultaneously: on the low-concentration side of the maximum, adsorption increases with rising concentration, but thereafter, this factor is outweighed by the shortage of single molecules caused by aggregation to form micelles.

We are not able clearly to correlate the contrast between these two types with any structural features of the respective simple molecules. There is obviously a change, increasing rapidly with concentration, which occurs to the solutes of Type II but not to

FIG. 5.



those of Type I: it becomes manifest by the falling off towards zero adsorption, and, but for its operation, the maximum adsorption attained in Type II would be greater than is actually the case. An aggregation would decrease the concentration in the same sense, and it is noteworthy that Congo-red (of Type II) is known to be highly micellular, whereas orange-II and methylene-blue (of Type I) are mainly simple in solution. Further, in so far as adsorption is due to polar influences, it is to be expected that the monomeric form of a given polar solute will be more adsorbed than a coupled polymeric form of it,

because a dipole-association which constitutes a polymeride of the type $\begin{smallmatrix}\ominus - +\\ + - \oplus\end{smallmatrix}$ necessarily makes the residual field of force less than that of the unassociated molecule.

The area of the interface occupied by the adsorbed molecule, reckoned as monomeric, in the region of maximum adsorption can be calculated from our measurements. From plane projections of the four compounds (Fig. 1) the areas of their simple molecules can be approximately assessed in sq. Å. These two sets of values are compared in Table I.

TABLE I.

		On benzene.		On chlorobenzene.	
Dye.	Area, calc.	Area found.	Ratio.	Area found.	Ratio.
Methylene-blue	140	215	1·5	215	1·5
Orange-II	112	180	1·6	180	1·6
Methyl-orange....................	79	218	2·8	40	0·5
Congo-red	192	470	2·5	117	0·6

Even when all allowance is made for the necessarily inexact calculated area, it remains evident that in the first two cases the adsorbed layer, on either interface, is unimolecular, with possibly some slight lateral scattering, such as interionic repulsions between neighbouring molecules of these compounds might well produce. It is not clear why the two interfaces should act equally in this respect.

In the second pair of cases, the surface distribution on benzene is definitely more sparse than in a single layer of contiguous molecules, whereas on chlorobenzene it is roughly twice as thick as this standard. That benzene, the less polar fluid, should adsorb in these two cases less than chlorobenzene, or alternatively allow more lateral movement of adsorbed polar molecules, is understandable; while the doubled surface concentration in these two instances clearly means either that the adsorbed molecules are not lying flat (being attached, for instance, by the attraction between their sodium ions and the chlorine atoms of the chlorobenzene) or that they are lying flat on the surface, but in layers of an average thickness of about two molecules.

Attempts to extend Lewis's experiments with sodium glycocholate were abandoned on account of the difficulty of purifying this substance.

EXPERIMENTAL.

A. *Adsorption at the Benzene–Water Interface.*—Benzene stored in a reservoir A (Fig. 6) flowed through a constant-pressure head B down a long tube C past a mercury trap D. It issued through a jet E, and rose in drops through the solution of the dye in the tube F. The drops passed out through an inclined tube at the top of F, which was only slightly larger than themselves, and into a reservoir G. There they coalesced with a layer of benzene which overflowed through a side tube H. The adsorbed layer was shed in G, and experiments showed that no appreciable diffusion back into F took place during the time occupied by an experiment (see below). The apparatus was of glass throughout.

The average duration of an experiment was about 20 hours, during which about 4 l. of benzene passed through in drops of volume about 0·1 c.c. issuing at a frequency of about 40 per minute. The average area of interface exposed in one experiment was about 3·5 sq. m. The rate of flow was determined by weighing the benzene overflowing in a measured time, and was maintained substantially constant by the constant-pressure head. The number of drops of benzene passing in a measured time was counted at frequent intervals. In order to prove that the surface was saturated (see below), the apparatus was constructed in duplicate, with columns of different lengths having jets of diameters 0·58 and 1·26 mm.

At the termination of each experiment the solution from G was run out and weighed, and its concentration compared in a Duboscq tintometer with that of a sample of the original solution. In order to obtain reproducible results, it was found necessary to carry out all the comparisons in direct bright sunlight. The experimental error quoted in Tables I and II, A—H, is inversely proportional to the difference in heights of the two liquid columns in the tintometer, and this set an upper limit to the concentrations which could be used, on account of the difficulty of comparing deeply coloured solutions differing only slightly from one another.

B. *Adsorption at the Chlorobenzene–Water Interface.*—In the case of chlorobenzene, similar sets of apparatus were used, but here the liquid fell in drops from jets C, of diameters 0·4 and

0·32 mm. dipping into solutions *D* (Fig. 7). After passing through a constriction *E*, the drops coalesced with the chlorobenzene surface *G* at the bottom of the reservoir *F*, in which the adsorbed dyestuff collected. (The chlorobenzene passed through one tap in the constant-pressure head; this was lubricated once with a very small quantity of rubber grease.) The chlorobenzene overflowed through a syphon *H*, and by adjusting the variable syphon limb *K* the height of the interface *G* could be kept constant. The volumes, drop numbers, and interfacial areas were similar to those given above for benzene.

FIG. 6.

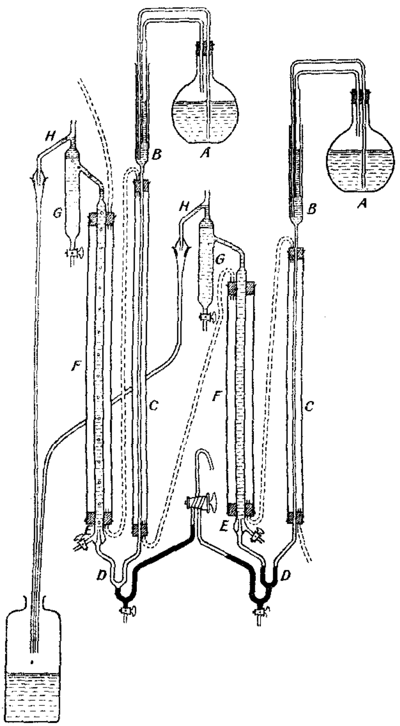
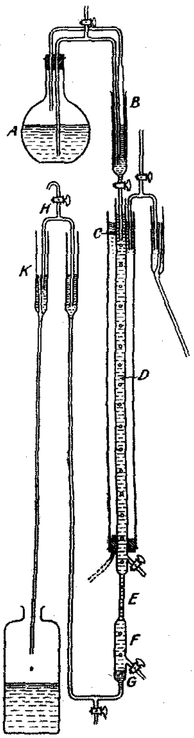


FIG 7.



Absence of Diffusion.—In order to test the possibility of diffusion of solute from the reservoi in which the adsorbed material had collected, the reservoir was filled with 0·088*N*-sodium chlorid solution, and the saturating column with distilled water. The sodium chloride solution los only 3·5% in concentration in 20 hours, and this value was unaltered even if benzene drop were passing up. The greatest concentration difference of dye set up in any experiment wa 0·000014 g.-mol./l., from which diffusion would be negligible.

The Interfacial Surface Area.—This was calculated from the total number of drops an

the total mass of organic liquid passing, the drops being assumed spherical and of uniform size. The former assumption is justified by the slow rate of movement of the drops—about 6 cm./sec.—and the latter by the observed constancy of the rate of flow, of the drop rate, and of the distances between successive drops in the adsorption columns.

TABLE II.

(A) *Methylene-blue on benzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·00436	1164	26,100	0·103 ± 0·007
0·0218	1035	29,070	0·85 ± 0·03
0·0436	900	41,800	1·6 ± 0·06
0·0550	1463	32,790	1·92 ± 0·07
0·0621	1862	50,240	2·18 ± 0·05
0·0653	810	27,580	2·11 ± 0·10
0·0872	1348	32,300	2·40 ± 0·10
0·1100	1250	40,880	2·41 ± 0·12
0·1310	818	37,920	2·40 ± 0·14
0·1960	1190	59,540	2·38 ± 0·06
0·4598	1292	32,680	2·6 ± 0·6
0·5475	1327	68,570	2·5 ± 0·3

(B) *Methylene-blue on chlorobenzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0210	1052	33,700	0·24 ± 0·01
0·0420	932	22,380	0·65 ± 0·03
0·0627	905	23,790	0·92 ± 0·04
0·0941	982	32,660	1·50 ± 0·05
0·1383	1148	28,910	1·74 ± 0·07
0·2074	893	32,320	2·0 ± 0·1
0·2879	1295	49,290	2·1 ± 0·1
0·4030	1292	34,290	2·4 ± 0·15
* {0·1177	1263	43,700	1·73 ± 0·05
{0·1177	1397	33,130	1·71 ± 0·05

(C) *Orange-II on benzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0191	1099	23,550	1·75 ± 0·03
0·0296	1506	30,020	2·61 ± 0·05
0·0411	1170	44,800	3·02 ± 0·04
0·0592	1405	33,160	3·25 ± 0·08
0·0823	1085	35,500	3·27 ± 0·04
0·0883	1383	38,560	3·38 ± 0·11
0·1183	975	26,370	3·25 ± 0·18
0·2006	847	29,200	3·37 ± 0·24
0·2057	3423	54,370	3·09 ± 0·11
0·3445	599	18,620	4·20 ± 0·67
0·4433	1394	33,500	3·21 ± 0·51
0·5890	1119	37,150	2·98 ± 0·74

(D) *Orange-II on chlorobenzene*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0298	1086	27,450	1·30 ± 0·02
0·0447	990	31,250	2·13 ± 0·03
0·0814	895	22,180	2·47 ± 0·06
0·1378	1077	26,800	2·55 ± 0·07
0·2444	861	21,230	2·90 ± 0·02
0·3353	1273	41,290	2·80 ± 0·10
0·5029	1142	36,440	2·9 ± 0·2
0·7071	1227	33,520	2·8 ± 0·3
1·0606	1098	35,490	3·6 ± 0·5
* {0·1995	1075	25,640	2·7 ± 0·1
{0·1995	577	24,770	2·8 ± 0·1

* Of this pair of figures the upper was obtained at 22° and the lower at 17°.

(E) *Methyl-orange on benzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·01332	1120	19,940	0·5 ± 0·03
0·0305	830	38,610	0·96 ± 0·04
0·0333	1163	28,150	1·12 ± 0·05
0·0500	591	18,100	1·9 ± 0·10
0·0800	1135	23,770	2·47 ± 0·10
0·0828	1263	49,430	2·21 ± 0·06
0·1093	851	26,750	2·50 ± 0·20
0·1332	1240	60,780	2·50 ± 0·10
0·2120	1448	43,610	1·63 ± 0·20
0·3278	1368	41,530	0·68 ± 0·34
0·5337	1364	41,470	—
1·0673	973	28,340	—

(F) *Methyl-orange on chlorobenzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0343	1243	46,020	4·16 ± 0·03
0·1308	1260	46,220	10·2 ± 0·1
0·2501	955	35,880	12·8 ± 0·1
0·3852	1073	39,900	13·0 ± 0·2
0·5022	930	23,410	11·5 ± 0·4
0·6816	1050	40,130	8·9 ± 0·2
1·1224	1300	54,500	5·3 ± 0·3
† {0·8155	1067	33,340	7·8 ± 0·3
{0·5826	1320	40,960	9·8 ± 0·2

† These two values were obtained at 22°.

(G) *Congo-red on benzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·01196	1498	24,770	1·56 ± 0·02
0·0239	1141	44,320	2·58 ± 0·02
0·0283	836	32,150	2·29 ± 0·05
0·0329	1013	32,460	2·45 ± 0·05
0·0423	1156	29,560	2·46 ± 0·05
0·0425	520	24,470	2·28 ± 0·08
0·0486	837	30,040	2·50 ± 0·07
0·0624	1446	34,620	2·21 ± 0·08
0·0729	953	32,270	1·75 ± 0·1
0·0851	882	33,680	0·57 ± 0·09
0·1276	1180	42,310	0·20 ± 0·1
0·1822	1181	33,170	—
0·1881	1164	31,850	—
0·3300	1556	46,390	—

(H) *Congo-red on chlorobenzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0205	1130	38,540	1·13 ± 0·01
0·0409	1130	36,140	1·08 ± 0·02
0·0629	1410	39,220	1·24 ± 0·03
0·0943	1230	42,640	1·59 ± 0·04
0·1425	912	24,610	3·18 ± 0·08
0·2503	1525	33,670	4·7 ± 0·1
0·3755	1380	38,880	6·8 ± 0·2
0·5247	1145	42,230	9·3 ± 0·2
0·6305	1047	24,110	9·6 ± 0·4
0·8000	965	25,150	9·2 ± 0·4
0·9608	876	30,210	4·9 ± 0·5
1·2000	913	31,800	1·1 ± 0·6
‡ {0·1981	1082	33,620	3·7 ± 0·1
{0·1981	1152	27,340	3·7 ± 0·1

‡ Of this pair of data the upper was obtained at 22° and the lower at 17°.

Proof of Saturation of the Surface.—With all dyes, two adsorption columns of different heights were used—125 cm. and 88 cm. for benzene, and 145 cm. and 100 cm. for chlorobenzene. The results obtained with the duplicate columns were found to be interchangeable within the

experimental error. The volume of the solution in the saturating column was at least eight times that of the reservoir, so the adsorption took place from a solution of virtually constant concentration.

Temperature Control.—Throughout the duration of the experiments the room temperature remained at 17° ± 1·5°. The apparatus was lagged with water jackets to minimise small fluctuations of temperature. With each dye, experiments with chlorobenzene were also carried out at 22°, and the results agreed, within the usual experimental error, with those of the same concentration at 17°.

Purity of Benzene and Chlorobenzene.—A. R. Benzene (Burgoyne, Burbidges, Ltd.) was used, but the results were unaffected by the substitution of benzene supplied as " Extra Pure." The chlorobenzene was B.D.H. " Purified."

Purification of the Dyes.—The test used as a criterion of the purity of all the dyes except methylene-blue was that the drop number of benzene against a solution of a particular concentration should be unaltered by further purification. Congo-red was salted out from aqueous solution four times with sodium acetate until free from chloride. It was then boiled with absolute alcohol, filtered off, and washed with alcohol until free from acetate as shown by the cacodyl test. Congo-red solutions faded on standing for several days, but not to any appreciable

FIG. 8.

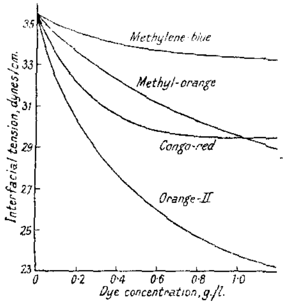
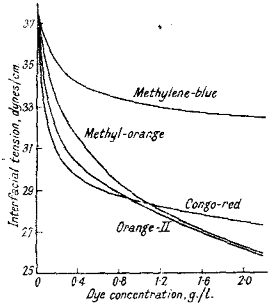


FIG. 9.



extent during the period of an experiment. All Congo-red solutions were made freshly for each experiment. Methyl-orange and orange-II were recrystallised from water respectively five and three times. Methylene-blue was free from zinc and sodium, the most probable impurities, and left no residue on ignition: it was therefore assumed to be pure.

Interfacial Tension Measurements.—Interfacial tensions between dye solutions and benzene and chlorobenzene were determined by the drop-number method, in which a constant volume of the organic liquid, 29·328 c.c., issued in drops from a pipette, the tip of which dipped below the surface of the aqueous solution. Decrease in the interfacial tension resulted in a decrease in the drop size and a corresponding increase in the number of drops, from 188 for chlorobenzene against pure water to 283 for the most concentrated solutions tested, and from 228 to 354 for benzene. The tips were drawn to circular apertures of diameter 0·082 and 0·092 cm. (measured on a travelling microscope) in the cases of benzene and chlorobenzene respectively. For the latter liquid it was necessary that the tip should be ground to a knife edge.

The rate of flow was controlled by a fine air leak, and was never greater than 5 drops per minute. The numbers were recorded automatically by the device described by us (*J. Sci. Instr.*, **1935**, **12**, 198).

The interfacial tensions were calculated from the drop numbers according to Harkins and Brown (*J. Amer. Chem. Soc.*, **1919**, **41**, 499), the necessary densities being taken from the International Critical Tables. Values of $d\sigma/dc$ were read from the smoothed graph of σ against c (Figs. 8 and 9).

A drop number against pure water was determined frequently, and gave 35·4 dynes/cm. for benzene and 37·4 dynes/cm. for chlorobenzene, at 17° ± 0·5°. For the present purpose these compare satisfactorily with those recorded in the International Critical Tables (Vol. IV,

436), *viz.* 35·2 (at 17°) and 37·41 dynes/cm. (at 20°) respectively, for the values of Γ are required only for comparison and do not affect the adsorption measurements. Furthermore, small errors in σ produce much smaller ones in $d\sigma/dc$.

These results, together with the values of the adsorption calculated from Gibbs's equation, are shown in Table III, and as broken curves in Figs. 2, 3, 4, and 5.

TABLE III.

Interfacial Tensions.

(A) *Methylene-blue–chlorobenzene.*

			Reading from σ–c curve.		
Concn., g./l.	Drop no.	σ, dynes/cm.	Concn., g./l.	$d\sigma/dc$.*	Adsorption, g./cm.^{2} × 10^8.
0·0000	188	37·41	0·1	10·1	1·34
0·0867	196	36·00	0·2	6·0	1·59
0·2167	202	34·95	0·3	4·2	1·67
0·4334	208	34·09	0·4	3·2	1·70
0·5778	210	33·72	0·6	1·85	1·47
1·0219	214	33·20	0·8	1·3	1·38
2·0438	219	32·50	1·0	1·0	1·33
			1·2	0·9	1·43
			1·4	0·75	1·39
			1·6	0·6	1·27
			1·8	0·5	1·19
			2·0	0·42	1·11

(B) *Orange-II–chlorobenzene.*

			Reading from σ–c curve.		
Concn., g./l.	Drop no.	σ, dynes/cm.	Concn., g./l.	$d\sigma/dc$.*	Adsorption, g./cm.^{2} × 10^8.
0·0000	188	37·41	0·08	21·8	2·53
0·0532	205	34·55	0·1	21·5	3·12
0·1064	213	33·35	0·12	20	3·48
0·2128	225	31·70	0·14	18	3·66
0·5319	240	29·86	0·16	14	3·48
1·0638	255	28·21	0·18	12·5	3·3
2·1275	283	25·58	0·2	11·1	3·22
			0·3	6·8	2·96
			0·4	4·7	2·73
			0·5	3·94	2·86

* Smoothed.

(C) *Methyl-orange–chlorobenzene.*

0·0000	188	37·41	0·1	18·2	2·47
0·1244	207	34·24	0·2	11·6	3·15
0·3111	222	32·08	0·3	8·7	3·54
0·6222	237	30·20	0·4	6·7	3·63
0·9334	248	29·00	0·6	4·85	3·95
1·2445	258	27·88	0·8	4·0	4·34
1·8667	273	26·47	1·0	3·4	4·61
			1·2	3·0	4·88
			1·4	2·6	4·94
			1·6	2·3	4·99
			1·8	2·0	4·88
			2·0	1·7	4·61

(D) *Congo-red–chlorobenzene.*

0·0000	188	37·41	0·02	43	2·49
0·0495	210	33·79	0·04	43	5·02
0·1503	228	31·32	0·06	37	6·34
0·1981	232	30·82	0·08	29	6·62
0·3962	241	29·73	0·10	23·5	6·71
0·6604	246	29·17	0·15	13·6	5·83
1·3208	256	28·10	0·20	8·1	4·63
1·9812	263	27·38	0·30	4·45	3·81
			0·40	3·17	3·62
			0·50	2·30	3·29

(E) *Methylene-blue–benzene.*

0·0000	228	35·4	0·1	3·875	0·519
0·1340	232·5	34·7	0·2	3·19	0·837
0·2681	236	34·4	0·3	2·65	1·056
0·5475	241	33·7	0·4	2·2	1·156
0·8580	244	33·4	0·5	1·81	1·190
1·0725	246	33·2	0·6	1·5	1·182
			0·7	1·25	1·149
			0·8	1·025	1·077
			0·9	0·875	1·034
			1·0	0·75	0·985

(F) *Orange-II–benzene.*

0·0000	228	35·4	0·1	21·0	3·02
0·1003	254	32·1	0·2	15·5	4·46
0·2006	271	30·3	0·3	12·5	5·39
0·3396	290	28·4	0·4	10·5	6·04
0·5230	311	26·6	0·5	9·0	6·47
0·6970	329	25·3	0·6	7·5	6·47
1·0460	354	23·6	0·7	6·25	6·29
			0·8	5·25	6·04
			0·9	4·5	5·88
			1·0	4·0	5·75

(G) *Methyl-orange–benzene.*

0·0000	228	35·42	0·1	8·8	1·184
0·1334	237·5	34·01	0·2	7·5	2·013
0·2669	245	33·13	0·3	6·63	2·67
0·5337	259	31·5	0·4	6·0	3·22
0·8518	273	30·0	0·5	5·4	3·64
1·0673	281	29·2	0·6	4·95	3·99
			0·7	4·55	4·25
			0·8	4·15	4·48
			0·9	3·90	4·71
			1·0	3·75	4·97

(H) *Congo-red–benzene.*

0·0000	228	35·4	0·1	15·5	4·43
0·0911	241	33·5	0·2	11·0	6·49
0·1254	243	33·4	0·3	8·25	6·86
0·1881	252	32·2	0·4	6·0	6·86
0·2370	257	31·7	0·5	4·5	6·07
0·3696	266	30·7	0·6	3·0	5·14
0·4435	271	30·3	0·7	1·75	3·50
0·6650	278	29·5	0·8	0·75	1·71
0·8308	280	29·4	0·9	0·25	0·64
1·0730	281	29·3	1·0	0·00	—

It is a pleasure to acknowledge the help we have received from Professor Irvine Masson's friendly criticism. One of us (C. C. A) is indebted to the Cumberland County Education Authority for a Major Scholarship and for a grant from the Edward Seton Chance Fund.

THE DURHAM COLLEGES IN THE UNIVERSITY OF DURHAM. [*Received, November 21st, 1935.*]

26. *The Resolution of Phenyl*-n-*propylcarbinol.*

By J. Kenyon and S. M. Partridge.

By fractional crystallisation of the strychnine salt of phenyl-*n*-propylcarbinyl hydrogen phthalate until the liberated hydrogen phthalic ester had reached a constant rotatory power ($[\alpha]_{5893}$ − 7·0° in ether) Levene and Marker (*J. Biol. Chem.*, 1932, **97**, 386) obtained *l*-phenyl-*n*-propylcarbinol with $[\alpha]_{5893}$ −35·8° (in benzene). For reasons which we hope to discuss in a forthcoming communication, we considered—in opposition to the view of Levene and Marker—that optical purity had not been reached. Accordingly we have re-examined the method of resolution.

By fractional crystallisation of its quinidine salt, phenyl-*n*-propylcarbinyl hydrogen phthalate was readily obtained with $[\alpha]_{5893}$ + 9·8° (in ether). When the highly lævorotatory hydrogen phthalic ester obtained from the more soluble fractions of the quinidine salt was converted into its strychnine salt, and this submitted to fractional crystallisation, the corresponding *l*-phenyl-*n*-propylcarbinyl hydrogen phthalate was obtained with $[\alpha]_{5893}$ − 10·0° (in ether).

Saponification of the *d*-acid ester yielded *d*-phenyl-*n*-propylcarbinol, m. p. 49°, b. p. 115°/14 mm., the rotatory powers of which are recorded in Table I. The rotatory powers of the various derivatives are given in Table II.

Table I.

Rotatory Power (l, 0·5) *and Refractive Index of* (+) *Phenyl*-n-*propylcarbinol.*

Temp.	43°	47·5°	50°	54°	56°	57°	60°	65°
α_{5780}	+ 15·86°	—	+ 16·42°	—	+ 16·75°	+ 16·75°	—	+ 17·11°
α_{5461}	+ 17·84°	—	+ 18·75°	—	+ 18·98°	+ 19·03°	—	+ 19·02°
α_{4358}	+ 30·52°	—	+ 31·66°	—	+ 32·40°	+ 32·51°	—	+ 33·06°
$n_D^{t°}$	—	1·5005	—	1·4989	—	—	1·4969	1·4945

Table II.

	Solvent.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
1. *d*-Phenyl-*n*-propylcarbinol	C_6H_6	4·791	+ 43·6°	+ 46·2°	+ 52·2°	+ 87·3°
,, ,, ...	CS_2	4·415	—	+ 55·72	+ 63·42	+ 108·7
2. *l*-Phenyl-*n*-propylcarbinol	C_6H_6	5·150	− 45·9	− 47·2	− 53·5	− 90·0
3. *d*-Phenyl-*n*-propylcarbinyl hydrogen phthalate	Et_2O	3·467	+ 9·8	+ 11·2	+ 11·5	+ 13·2
4. *l*-Phenyl-*n*-propylcarbinyl hydrogen phthalate	Et_2O	4·721	− 10·0	− 10·9	− 11·0	− 13·5
5. Quinidine salt of (3)	$CHCl_3$	2·08	—	+ 140·0	+ 181·0	+ 322
6. Strychnine salt of (4)	$CHCl_3$	0·538	− 37·2	—	− 40·9	− 112·4

Experimental.

Phenyl-*n*-propylcarbinol, b. p. 117—118°/18 mm., m. p. 16°, $d_{4°}^{16·2°}$ 0·9822, $d_{4°}^{26·3°}$ 0·9739, $d_{4°}^{37·0°}$ 0·9654, $d_{4°}^{46·7°}$ 0·9582, $n_D^{22°}$ 1·5166 (Grignard, *Ann. Chim. Phys.*, 1901, **24**, 466, gives b. p. 113°/10 mm., $d_{4°}^{13·7°}$ 0·9861, $n_D^{13·7°}$ 1·51914), obtained in 69% yield by the Grignard reaction, was smoothly converted into its hydrogen phthalic ester, which formed clusters of small needles, m. p. 90—91°, from carbon disulphide and light petroleum (Found, by titration with sodium hydroxide: *M*, 297·6. $C_{18}H_{18}O_4$ requires *M*, 298).

Quinidine (200 g.) was dissolved in a solution of the hydrogen phthalic ester (171 g.) in acetone (1000 c.c.). The salt, which separated at once, was only sparingly soluble in hot acetone and was recrystallised from ethyl acetate (9 l.), forming rosettes of woolly needles (132 g.), m. p. 168—169°; a further crop (30 g.) of the optically pure salt was obtained by concentration of the second mother-liquor.

The more soluble fractions of the quinidine salt yielded a somewhat pasty *l* + *dl*-hydrogen phthalic ester (35 g.), which was combined with strychnine (38 g.) in methyl-alcoholic solution (180 c.c.). The strychnine salt, after two recrystallisations from methyl alcohol, was obtained in rosettes of needles (40 g.), m. p. 184—185° (decomp.). *d*-Phenyl-*n*-propylcarbinyl hydrogen phthalate, from the less soluble quinidine salt, separated from carbon disulphide–light petroleum

in long needles, m. p. 53—54°; the corresponding *l*-phenyl-*n*-propylcarbinyl hydrogen phthalate, m. p. 52—53°, was obtained from the less soluble strychnine salt.

d-Phenyl-*n*-propylcarbinol, obtained by saponification of the *d*-hydrogen phthalic ester by aqueous-alcoholic sodium hydroxide, solidified with remarkable readiness to a mass of long needles, m. p. 49°, b. p. 115°/14 mm. The corresponding *l*-alcohol had m. p. 48—49°.

d-Phenyl-*n*-propylcarbinyl acetate, b. p. 125°/16 mm., obtained by heating the *d*-alcohol with acetic anhydride in pyridine solution, had $n_D^{20.5°}$ 1·4889 and $\alpha_{5780}^{20°}$ + 26·96°, $\alpha_{5461}^{20°}$ + 30·85°, $\alpha_{4358}^{20°}$ + 55·35° (*l*, 0·25) (Grignard, *loc. cit.*, gives b. p. 117—118°/8 mm.).

Thanks are due to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Ltd. for grants and to Mr. B. C. Platt for assistance in the preparation of material.

BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, November 26th*, 1935.]

27. *The Planar Configuration of Quadricovalent Compounds of Bivalent Copper and Nickel.*

By E. G. COX, E. SHARRATT, W. WARDLAW, and K. C. WEBSTER.

IN a recent communication by two of us (J., 1935, 731) it was shown that, in a number of 4-covalent compounds of bivalent copper, the metal valencies are coplanar, as in bivalent nickel, palladium, and platinum. Further support for this view has been obtained by

FIG. 1.

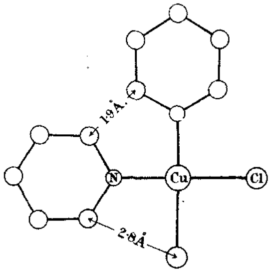
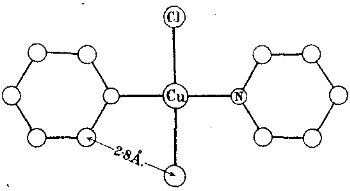


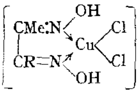
FIG. 2.

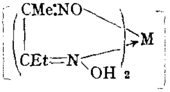


an investigation of the simple derivative, dipyridinocupric chloride, Cu py_2Cl_2. This substance, which crystallises well from methyl alcohol, has been prepared under various experimental conditions with the object of discovering the theoretically possible *cis*- and *trans*-isomerides. Under all conditions, we find that it crystallises in the same form, which possesses a *trans*-planar configuration. This result follows from a consideration of the cell dimensions of the substance as determined by *X*-ray methods. The short length of the *c*-axis (3·84 Å.) shows that the two pyridine rings must be coplanar (or very nearly so), since its value is of the same order as the distance of approach of =CH– groups in different molecules. Reference to a model shows that this can only be so in a molecule of *trans*-planar configuration, for with a *cis*-planar configuration the parallel arrangement of the pyridine rings shown in Fig. 1 is impossible on account of the proximity of the two rings (minimum distance 1·9 Å. instead of 3·7 Å.). In order to obtain the requisite clearance between the rings, they must be rotated about the N–Cu bonds through approximately 40°, thus increasing the thickness of the molecule and necessitating a *c*-axis of at least 4·5 Å. On the same grounds, a molecule in which the distribution of copper valencies is

tetrahedral is excluded: in this case the projection of the chlorine atoms in a plane at right angles to that of the nitrogens would also exclude so short a *c*-axis as 3·8 Å. The molecule therefore has a planar *trans*-configuration in which the pyridine rings are coplanar: as Fig. 2 shows, however, the rings are probably rotated slightly out of the plane of the copper valencies (while remaining parallel to each other) in order that the minimum Cl–CH distance may be about 3·0 Å.

The inability to obtain the *cis*-derivative recalls the similar difficulty experienced with palladium, which from aqueous solutions yields only a *trans*-derivative, Pd py_2Cl_2, by the use of pyridine: although, in the latter case, a *cis*-compound can be obtained by using potassium chloropalladite and pyridinium acetate (Grünberg, *Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 218; *A.*, 1934, 379), yet it readily reverts to the α(*trans*)-form. That the *cis*-form of the copper salt is also very unstable has been clearly demonstrated by a reaction between pyridine and a copper compound in which the chlorine atoms must be in *cis*-positions. We have isolated as green crystalline substances four complex *salts* of the type (I), where

(I.) 

 (II.)

R = H, CH_3, C_2H_5, or $C_6H_5{\cdot}CH_2$; these 4-covalent compounds were readily soluble in alcohols, in acetone, and (except the first) in chloroform and benzene. Furthermore, *copper methylglyoxime dichloride* (I; R = H) was found to be unimolecular in acetone and phenol, and to have a negligible electrical conductivity in the former solvent. A crystallographic study of the dimethylglyoxime compound (I; R = CH_3) strongly suggests a planar form for this substance.

Addition of pyridine to a solution of any of these substances in alcohol or acetone displaces the oxime, and must form *cis*-Cu py_2Cl_2 initially. However, the product isolated is always the *trans*-planar form. Quadricovalent copper compounds of *cis*-configuration, like those of palladium, are therefore undoubtedly unstable when chelate groups are absent.

Since the distribution of valencies is planar in both cases, and the metal atoms are not greatly different in radius, it is to be expected that corresponding copper and nickel compounds will sometimes be isomorphous. This has proved to be the case with the methylethylglyoxime *derivatives* (II; M = Cu or Ni). These substances are microcrystalline, but microscopic examination and *X*-ray powder photographs show that they are undoubtedly isomorphous. The table (p. 133) shows the close correspondence between the lattice spacings of the two derivatives. Theoretically, these compounds should exist in *cis*- and *trans*-modifications, but an examination of the products resulting from interaction of the oxime with the acetates of nickel and copper has shown that only one substance is obtained. Again, as both substances were decomposed by heat, without melting, it is not possible to obtain isomerides of them as Sugden (*J.*, 1932, 246; 1935, 621) was able to do in the case of the nickel derivatives of some other unsymmetrical oximes.

Experimental.

Methylglyoxime.—This was prepared by Tschugaeff's method (*Chem. Zentr.*, 1911, **82**, i, 871). Acetoacetic ester (90 g.), sodium nitrite (50 g.), and potassium hydroxide (42 g.) were dissolved in water (1800 c.c.), and the pale yellow mixture kept over-night; it was then cooled to 0°, air was bubbled through it, and 5*N*-sulphuric acid (*ca.* 150 c.c.) added slowly until it was acid to methyl-orange. After standing for an hour (still at 0°), the mixture was extracted with ether (5 × 100 c.c.), the ether removed, and the resulting *iso*nitrosoacetone dried in a vacuum desiccator; yield, 46 g. The whole of this product was dissolved in sodium hydroxide solution (46 g.; 200 c.c.), and hydroxylamine hydrochloride (100 g.) added. The mixture was warmed on the water-bath for 2 hours; on cooling, white crystals of methylglyoxime separated; yield, 44 g.; m. p. 154° (Found: N, 27·8. Calc. for $C_3H_6O_2N_2$: N, 27·5%).

Methylethylglyoxime.—Ethyl ethylacetoacetate ("Organic Syntheses," Vol. VII, p. 36) was converted into methyl *iso*nitrosopropyl ketone by the method described above. Intro-

duction of the second oxime group was also effected similarly. The oxime, which was much more readily soluble than dimethylglyoxime in alcohol, melted at 170—171° (Schramm, *Ber.*, 1883, **16**, 181, gives 170°).

Benzylmethylglyoxime.—Ethyl benzylacetoacetate was synthesised by a method similar to that for the ethyl derivative. The glyoxime was then prepared by Sugden's method (J., 1932, 249). Our oxime melted at 183°; Sugden gives 194°, but Schramm (*loc. cit.*) gives 180—181°.

Copper Methylglyoxime Dichloride (I; R = H).—A cold alcoholic solution of anhydrous copper chloride (7 g.; 150 c.c.) was mixed with methylglyoxime (5 g.) dissolved in alcohol (50 c.c.). Sap-green crystals of the *dichloride* began to appear almost immediately, and were removed after an hour. They were washed with a little alcohol and dried; m. p. 156° (decomp.) (Found: Cu, 26·8; Cl, 29·7; C, 15·45; H, 2·6; N, 11·8. $C_3H_6O_2N_2,CuCl_2$ requires Cu, 26·9; Cl, 30·0; C, 15·2; H, 2·5; N, 11·8%). The substance was soluble in alcohols and acetone, but was decomposed by the addition of cold water, with the liberation of some of the oxime. The results of the molecular-weight determinations and of electrical conductivity measurements in acetone leave no doubt that this substance is a true 4-covalent compound:

Cryoscopic determination in phenol (constant = 7·27° per 1000 g.). 10·54 G. per 1000 g. gave Δt = 0·318°, whence M = 241 (Calc.: 236).

Ebullioscopic determination in acetone (constant = 2·22° per litre). 16·90 G. per 1000 c.c. gave Δt = 0·158°, whence M = 237.

Conductivity.—A solution of the dichloride in acetone (7·384 g./l.) had $\kappa = 8{\cdot}74 \times 10^{-5}$ mho at 25°, whence μ = 2·80.

Copper Dimethylglyoxime Dichloride (I; R = CH_3).—Cold alcoholic solutions of anhydrous copper chloride (2 g.; 80 c.c.) and dimethylglyoxime (2 g.; 120 c.c.) were mixed. Deep green crystals of the required compound separated rapidly; they were washed with alcohol and dried (Found: Cu, 25·44; Cl, 28·39; N, 10·8. Calc. for $C_4H_8O_2N_2,CuCl_2$: Cu, 25·39; Cl, 28·34; N, 11·18%). This substance was also prepared by warming to 60°, for 5—7 minutes, aqueous cupric chloride (10 g.; 100 c.c.) and solid dimethylglyoxime (3 g.). When the deep green solution was filtered and allowed to cool, it deposited crystals of the dichloride (Found: Cu, 25·40%). It is important not to wash this product with pure water since this causes decomposition, the oxime separating from the mixture. This compound had been prepared by Paneth and Thilo (*Z. anorg. Chem.*, 1925, **147**, 196) by passing dry hydrogen chloride over dry copper dimethylglyoxime; these authors considered the chlorine atoms to be ionised, since the halogen could be precipitated with cold alcoholic silver nitrate; but since this reagent contains water, which decomposes the product, this reaction provides no evidence as to the structure of the compound, which is clearly similar to that of the methylglyoxime derivative just described. Again, this substance is soluble in chloroform and benzene.

If copper dimethylglyoxime dichloride is boiled with water for 10 minutes, or aqueous cupric chloride (10 g.; 150 c.c.) is boiled with dimethylglyoxime (5 g.) for 15 minutes, cuprous chloride separates, and if this is removed, and the filtrate cooled, fine yellow needles are deposited. These are very readily oxidised by air, and for analysis they were removed in an atmosphere of nitrogen (Found: Cu, 27·7; Cl, 17·6. $C_4H_8O_2N_2$,CuCl requires Cu, 29·6; Cl, 16·5%); they appear, therefore, to be the *cuprous* derivative.

Copper Methylethylglyoxime Dichloride (I; R = C_2H_5).—When cold alcoholic solutions of methylethylglyoxime (3 g.; 40 c.c.) and anhydrous cupric chloride (3 g.; 50 c.c.) were mixed, emerald-green crystals of the required *compound* separated rapidly; they were removed and dried (Found: Cu, 24·0; Cl, 26·65. $C_5H_{10}O_2N_2,CuCl_2$ requires Cu, 24·0; Cl, 26·8%). This compound resembles the dimethyl derivative in its solubility in organic solvents. Water decomposes it, with liberation of the original oxime.

Copper Benzylmethylglyoxime Dichloride (I; R = CH_2Ph).—Cold alcoholic solutions of the glyoxime (3 g.; 60 c.c.) and anhydrous cupric chloride (3 g.; 60 c.c.) were mixed. The complex, which separated almost immediately, crystallised in pale green leaflets possessing a silvery reflex. Its properties were similar to the two compounds just described (Found: Cu, 19·3; Cl, 21·45. $C_{10}H_{12}O_2N_2,CuCl_2$ requires Cu, 19·5; Cl, 21·7%).

Reaction of Pyridine with the Glyoxime Compounds of Cupric Chloride.—Solutions of these glyoxime derivatives of cupric chloride (I) in acetone or alcohol, at 15°, were treated with pyridine. From the methylglyoxime compound, dipyridinocupric chloride separated almost immediately in pale blue, microscopic needles. These were removed and examined by X-ray powder photographs without recrystallisation, so as to preclude any possibility of the product reverting to a more stable isomeride, for it is well known that recrystallisation of *cis*-dipyridinopalladium chloride effects such a transformation. This reaction was also carried out at − 10°,

but a similar product was obtained [Found, for compound formed at 15°: Cu, 21·5; Cl, 23·8; for compound formed at − 10°: Cu, 21·5. Calc. for $Cu(C_5H_5N)_2Cl_2$: Cu, 21·7; Cl, 24·2%]. Addition of pyridine to the other glyoxime derivatives also produced the same compound, but the reaction was much slower in these cases, especially when the dimethylglyoxime compound was used (Found, from dimethyl compound: Cu, 21·4; from methylethyl compound: Cu, 20·9; from benzylmethyl compound: Cu, 20·8%). The last two derivatives were contaminated with a little of the hexapyridinocupric chloride.

Dipyridinocupric Chloride.—This substance was then prepared by Lang's method (*Ber.*, 1888, **21**, 1580), *i.e.*, by the direct action of pyridine on cupric chloride in alcoholic solution; it crystallised from methyl or ethyl alcohol in fine blue needles (Found: Cu, 21·7%). Addition of acetic acid to the alcoholic copper chloride did not affect the product obtained on the addition of pyridine, even when the reaction was effected at − 10°.

Copper Bismethylethylglyoxime (as II).—An aqueous solution of copper acetate (1 g.; 100 c.c.) was acidified with a few drops of acetic acid, and an alcoholic solution of methylethylglyoxime (1·3 g.; 50 c.c.) added. After being heated for 30 minutes, the solution was filtered and cooled; dark brown microscopic needles then separated; m. p. 179° (decomp.) [Found: Cu, 19·8. $(C_5H_9O_2N_2)_2Cu$ requires Cu, 19·8%]. A saturated solution of *copper bismethylethylglyoxime* in chloroform or benzene was fractionally precipitated with light petroleum. All fractions melted at the same temperature as the original, *viz.*, 179° (decomp.). When plunged in an oil-bath at 175°, none of the fractions melted, showing that the true m. p.'s had been recorded (cf. Sugden's experiments with the nickel compounds, *loc. cit.*).

This compound was also prepared by the addition of cold aqueous copper acetate (1 g.; 25 c.c.) to an alcoholic solution of the oxime (1·3 g.; 50 c.c.). Cold water (50 c.c.) was then added, and after being stirred for a few minutes, the mixture was filtered. On standing, the filtrate deposited dark brown needles, which were much larger than those prepared by the previous method; they were, however, otherwise identical; m. p. 179° (decomp.). This substance was soluble in organic solvents, but did not give good crystals on recrystallisation.

Nickel Bismethylethylglyoxime.—Methylethylglyoxime (1 g.) was dissolved in warm alcohol (140 c.c.) and added to a hot aqueous solution of nickel sulphate (2 g.; 200 c.c.) containing a few drops of dilute sulphuric acid. Ammonia was then added slowly, till precipitation was complete. After the hot solution had stood for an hour, the tangerine-coloured *complex* was removed, and dried in an oven [Found: Ni, 18·35. $(C_5H_9O_2N_2)_2Ni$ requires Ni, 18·5%]. A remarkable feature of this substance was its ready solubility in alcohols and benzene, in which it was about 50 times as soluble as nickel dimethylglyoxime. Attempts to isolate two isomerides of this substance failed; all fractions obtained from acetone–water decomposed at the same temperature as the original, *viz.*, 260°.

Reaction between Copper Acetate and Methyl- or Benzylmethyl-glyoximes.—When either of these glyoximes was used in place of methylethylglyoxime in the preparation of a copper derivative as above, the product was of a different type: only one oxime group was associated with the metal atom, which had replaced the hydrogen atoms from both oxime groups of the glyoxime. The *substances* were black and hygroscopic, analysis indicating that they were hydrated (Found for methylglyoxime compound: Cu, 35·8. $C_3H_4O_2N_2Cu,H_2O$ requires Cu, 35·0%; for benzylmethylglyoxime compound: Cu, 21·2. $C_{10}H_{10}O_2N_2Cu,2H_2O$ requires Cu, 21·9%). These compounds are evidently similar to the α-benzoinoxime derivative of copper which we recently studied (J., 1935, 818). They were not further examined, as they were of no use for stereochemical purposes.

Crystallographic and X-Ray Results.

X-Ray investigations were carried out by means of single-crystal rotation and oscillation photographs using copper K_α radiation.

Copper Dimethylglyoxime Dichloride.—This compound forms triclinic combinations of $a\{100\}$, $b\{010\}$, $c\{001\}$, and $p\{0\bar{1}1\}$; tabular on $b\{010\}$, and sometimes elongated along $[c]$. Angles observed: $a(100):b(010) = 64°\ 17'$; $b(010):c(001) = 69°\ 37'$; $c(001):p(0\bar{1}1) = 51°\ 35'$. From *X*-ray measurements, $a = 7·96$, $b = 8·10$, $c = 7·54$ Å., $\alpha = 100°\ 23'$, $\beta = 109°\ 52'$, and $\gamma = 109°\ 18'$.

The crystals are non-pyroelectric, and there are two molecules in the unit cell (*d*, calc. = 2·00 g./c.c.; obs. = 1·98). The space-group is therefore $P\bar{1}$ (C_i^1) and the molecules asymmetric.

Optical properties: the minimum refractive index in the (010) plane is 1·57 ($\lambda = 5461$) and is inclined at 29° to the *a*-axis in the obtuse angle β. The birefringence is very high, the maximum index not being accurately measurable owing to strong absorption.

These results, combined with the observation that the *a*-axis rotation photograph shows weak odd-layer lines, strongly suggest that the molecules are flat and equally spaced along the *a*-axis, so that their thickness is approximately $\frac{1}{4}a$.cos 29°, *i.e.*, 3·5 Å.

Dipyridinocupric Chloride.—This substance crystallises in poorly developed monoclinic combinations of $a\{100\}$, $m\{110\}$, and $p\{011\}$, greatly elongated parallel to $[c]$. Refractive indices : α (parallel to $[c]$) = 1·60, γ = 1·75 (λ = 5461). Strongly dichroic.

X-Ray measurements give a = 34·0 ± 0·5, b = 8·4 ± 0·1, and c = 3·84 ± 0·05 Å. The angle β is apparently close to 90°. With four molecules in the unit cell, d = 1·76 g./c.c. (obs. 1·76). The space-group was not determined, but the lattice is probably uncentred, and the absence of pyroelectric effects shows the class to be C_{2h} or C_s.

Copper Bismethylethylglyoxime.—This compound forms very small dark brown elongated plates, having a rhomboidal outline with an angle of 58°. The slow vibration is inclined at about 48° to the direction of elongation in the acute angle of the rhomboid. An *X*-ray powder photograph was taken with copper K_α radiation in a camera of 3 cm. radius; the measured spacings (in Å.) are recorded in the table.

Nickel Bismethylethylglyoxime.—This substance forms small red crystals of the same appearance as those of the copper derivative (angle of rhomboid 58°, slow vibration inclined at approx. 43° to the direction of elongation). The lattice spacings measured in the same way as for the copper derivative are shown in the table (I = intensity).

Copper compound.				Nickel compound.			
d.	*I.*	*d.*	*I.*	*d.*	*I.*	*d.*	*I.*
8·50	v.s.	3·10	v.w.	8·50	v.s.	—	—
7·18	v.w.	2·91	m.s.	7·13	v.w.	2·92	s.
6·00	m.s.	2·70	m.s.	6·00	m.w.	2·70	m.w.
5·36	m.s.	2·53	v.w.	5·33	m.w.	2·51	m.w.
4·68	m.	2·32	m.	4·63	v.w.	2·32	m.
4·08	s.	2·09	m.	4·09	s.	2·08	m.
3·69	s.	1·87	m.	3·72	s.	1·86	m.
3·50	s.			3·52	m.		

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THE UNIVERSITY, BIRMINGHAM, 15. [*Received, November 5th*, 1935.]

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28. *The Effect of Temperature on the Ionisation Constants of Some Dibasic Acids.*

By ISLWYN JONES and F. G. SOPER.

IN Bjerrum's quantitative treatment (*Z. physikal. Chem.*, 1923, **106**, 219) of the relative ionisation constants of symmetrical dibasic acids, the potential at a distance r from an ionised carboxyl group was taken as $-q/\varepsilon r$, q being the electronic charge and ε the dielectric constant. More accurate treatment of the potential as a function of distance has been made by Ingold (J., 1931, 2179). Debye had obtained as a first approximation for the average moment of a molecule, $\overline{m}$, in the direction of an electric field, $\overline{m} = \gamma F + \mu^2 F/3kT$, where γ is the polarisability of the molecule and F the inner field acting on the molecule. This leads to the following expression connecting dielectric constant with electric moment :

$$(\varepsilon - 1)/(\varepsilon + 2) = 4\pi\nu(\gamma + \mu^2/3kT)/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If, however, the average moment of a molecule in the direction of the field is expanded to its next term,

$$\overline{m} = \gamma F + \mu^2 F/3kT - \mu^4 F^3/45k^3T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the Clausius–Mosotti expression becomes

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{D - E}{D + 2E} = \frac{4\pi\nu}{3}\left[\gamma + \frac{\mu^2}{3kT} - \frac{1}{45}\frac{\mu^4 F^2}{k^3T^3}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ν is the number of molecules per c.c., E the electric intensity, and D the induction at any point in the field. Ingold (*loc. cit.*) expressed E in terms of D by means of (3), expanded the expression in D as far as D^3, and replaced it by its equivalent q/r^2. In this way an expression for E was obtained as a function of r, and since potential, ϕ, is equal to $-dE/dr$, integration of the expression for E gave

$$\phi_1 = \frac{1 - \frac{4}{3}\pi\nu(\gamma + \mu^2/3kT)q}{1 + \frac{8}{3}\pi\nu(\gamma + \mu^2/3kT)r} + \frac{\frac{4}{5}\pi\nu\mu^4 q^3/45k^3T^3}{[1 + \frac{8}{3}\pi\nu(\gamma + \mu^2/3kT)]^4 r^5} \quad . \quad . \quad . \quad (4)$$

This may be compared with Bjerrum's expression where

$$\phi_B = q/\varepsilon r = [1 - \frac{4}{3}\pi\nu(\gamma + \mu^2/3kT)]/[1 + \frac{8}{3}\pi\nu(\gamma + \mu^2/3kT)]$$

Ingold further considered effects due to the compressibility of the solvent and to anisotropy, and derived numerical equations in which these effects are allowed for. These corrections, however, are of minor importance at distances of 4 Å. and over, as is shown by comparison of the values of ϕ_2, corrected for these other effects with those of ϕ_1, calculated from equation (4):

r, Å.	3·0	3·5	4·0	4·5	5·0	5·5	6·0	6·5	7·0
$\phi_1 \times 10^4$	7·67	4·35	2·86	2·10	1·06	1·38	1·19	1·06	0·952
$\phi_2 \times 10^4$ (Ingold)	6·73	4·17	2·83	2·08	1·65	1·38	1·19	1·06	0·952

Hence, when dealing with dibasic acids whose ionising centres are at distances apart of 4·0 Å. or more, we may ignore the corrections for anisotropy and compressibility without introducing appreciable error. It is thus possible, using (4), to obtain ϕ as a function of r at different temperatures, and so to obtain the distances apart of the ionising centres in the dibasic acid over a range of temperature.

In the evaluation of ϕ, the polarisability has been assumed to be independent of temperature, and μ has been evaluated from (1), ε being taken as $80 - 0{\cdot}4(t - 20°)$. This gives for $\mu \times 10^{18}$ at 25°, 50°, and 74°, the values 0·7611, 0·7920, 0·8220, respectively, and for the potentials

$$\phi_{25°} = 6{\cdot}112 \times 10^{-12}/r + 1{\cdot}368 \times 10^{-41}/r^5$$
$$\phi_{50°} = 7{\cdot}025 \times 10^{-12}/r + 1{\cdot}268 \times 10^{-41}/r^5$$
$$\phi_{74°} = 8{\cdot}159 \times 10^{-12}/r + 1{\cdot}194 \times 10^{-41}/r^5 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The value of the potential is obtained from Bjerrum's relation connecting the two ionisation constants of the acids, *viz.*, $\log K_1/K_2 - \log 4 = q\phi/2{\cdot}303kT$, and from this value of the potential, r is then obtained from (5).

In the present paper, the following symmetrical dibasic acids have been examined: *cis*- and *trans*-caronic, *cis*- and *trans*-hexahydroterephthalic, succinic, glutaric, β-methylglutaric, ββ-dimethylglutaric, β-*iso*propylglutaric, *cyclo*hexane-1 : 1-diacetic, adipic, *r*-βγ-diphenyladipic. The ionisation constants were determined electrometrically in cells without liquid junction (Harned and Robinson, *J. Amer. Chem. Soc.*, 1928, **50**, 3157), and the constants evaluated by the method of Kolthoff and Bosch (*Rec. trav. chim.*, 1928, **47**, 861).

Experimental.

The cell H_2(Pt)|Acid + NaOH, 0·001*M*-NaCl|AgCl,Ag was of a type already described (Jones and Soper, *J.*, 1934, 1836). All silver–silver chloride electrodes were tested before use by immersion in *N*/10-potassium chloride solution connected with an *N*/10-calomel electrode, the *E.M.F.* of the resulting combination being 0·0451 ± 0·0002 volt at 25°. *E.M.F.* readings were corrected to a total pressure of 760 mm., *i.e.*, to a hydrogen pressure of $760 - p_{H_2O}$, where p_{H_2O} is the vapour pressure of water at the particular temperature. In order to convert *E.M.F.* readings into hydrogen-ion concentration, the *E.M.F.*, $E_{0{\cdot}001}$, of the cell H_2(Pt)|0·001*M*-HCl| Ag,AgCl was examined from 25° to 76·7° (Jones and Soper, *loc. cit.*), whence

$$-\log c_H = (E_1 - E_{0{\cdot}001})/0{\cdot}0001983T + 3{\cdot}000 + 2\log f_1/f_{0{\cdot}001}$$

The activity coefficients were evaluated at the required temperatures as previously described for tartaric acid (*loc. cit.*).

Results obtained in a typical series of experiments are given in the following table, the *E.M.F.* data referring to a temperature of 25°. K_1^c and K_2^c represent the primary and the secondary concentration ionisation constant respectively.

trans-Caronic acid.

H_2A $\times 10^3$.	NaOH $\times 10^3$.	*E.M.F.*	$K_1^c \times 10^4$. 25°.	50°.	74°.	NaOH $\times 10^3$.	*E.M.F.*	$K_2^c \times 10^6$. 25°.	50°.	74°.
10·0	5·0	0·6250	1·69	1·47	1·19	15·0	0·7064	8·15	6·33	4·83
5·0	2·5	0·6259	1·72	1·38	1·10	7·5	0·7092	7·25	5·43	4·21
2·5	1·25	0·6288	1·76	1·35	1·08	3·75	0·71296	6·25	4·92	3·73
1·25	0·625	0·6327	1·67	1·32	1·07	1·875	0·7147	5·81	4·50	3·55

Results obtained for the various thermodynamic ionisation constants are recorded below the mean deviations from the mean values approximating to 1% :

Temp.	$10^5K_1^a$.	$10^8K_2^a$.	K_1^a/K_2^a.	*r*, Å.	Change in *r*, %, for 25—74°.	$10^5K_1^a$.	$10^8K_2^a$.	K_1^a/K_2^a.	*r*, Å.	Change in *r*, %, for 25—74°.
	cis-Caronic acid.					ββ-Dimethylglutaric acid.				
25°	459	0·494	931,000	2·59	—	20·1	45·7	440	3·55	—
50	380	0·446	852,000	—	—	1·28	32·6	393	—	—
74	283	0·381	743,000	—	—	9·33	25·2	370	—	—
	*cyclo*Hexane-1 : 1-diacetic acid.					*trans*-Caronic acid.				
25	32·5	10·85	2995	3·18	—	15·2	478	31·8	4·85	—
50	24·25	9·09	2668	—	—	12·1	358	33·8	4·78	2·9
74	17·9	7·80	2295	—	—	10·3	264	39·0	4·71	—
	Succinic acid.					Glutaric acid.				
25	6·89	247	28·0	4·98	—	4·58	389	11·78	7·18	—
50	7·33	230	31·9	4·90	4·0	4·41	343	12·85	6·98	6·8
74	7·37	188	39·2	4·78	—	3·69	247	14·94	6·69	—
	β-Methylglutaric acid.					β-*iso*Propylglutaric acid.				
25	5·61	391	14·35	6·38	—	5·05	308	16·40	5·95	—
50	5·17	318	16·26	6·11	7·8	4·63	237	19·51	5·64	8·6
74	4·29	223	19·24	5·88	—	3·87	167	23·17	5·44	—
	Adipic acid.					*r*-βγ-Diphenyladipic acid.				
25	3·70	386	9·58	8·51	—	6·04	639	9·47	8·69	—
50	3·29	322	10·22	8·38	4·7	5·31	467	11·37	7·64	16·0
74	2·90	255	11·40	8·11	—	3·97	305	13·03	7·30	—

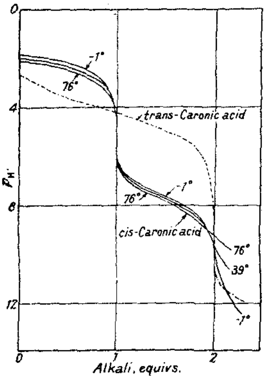
The *trans-dl*-caronic acid, m. p. 212°, and the *cis*-caronic acid, m. p. 178°, were kindly presented by Professor J. L. Simonsen, F.R.S., as was also the anhydride of β-*iso*propylglutaric acid from which the acid, m. p. 102°, was prepared. The diphenyladipic acid was kindly presented by Dr. G. R. Ramage. β-Methylglutaric acid (m. p. 88°), ββ-dimethylglutaric acid (m. p. 102°), and *cyclo*hexane-1 : 1-diacetic acid (m. p. 181°) were prepared by standard methods. Succinic, glutaric, and adipic acids were commercial products thrice recrystallised from conductivity water.

Discussion.

According to Baeyer (*Ber.*, 1896, **29**, 2797), *cis*-caronic acid titrates sharply monobasic at room temperature (indicator not specified), whilst at − 2° it titrates as a dibasic acid. The electrometric titration of this acid was suggested by Professor J. L. Simonsen, and the results are in Fig. 1, which compares the *cis*- and the *trans*-acid and shows the effect of temperature on the p_H changes during neutralisation of the former. The curves were shown to be reversible by back titration with acid. No marked displacement of the curve of the *cis*-acid occurs with change of temperature, and with phenolphthalein no indication of monobasicity is obtained at room temperature. With an indicator of lower p_H range the acid would titrate sharply monobasic, but it is unlikely that Baeyer used such an indicator in view of his reference to Bredt's work on camphoronic acid (*Annalen*, 1896, **292**, 83), in which phenolphthalein was employed. The effect of temperature on the inflexion point at the second neutralisation stage is marked. The second ionisation constant of the *cis*-acid is 0·49 × 10^{-8}, and the disappearance of the inflexion is due to increased

hydrolysis of the salt attendant on the 200% increase of K_w over the temperature range 0—70°. *To secure a sharp end-point in the titration of such weak acids, titration should be made at low temperatures.*

FIG. 1.

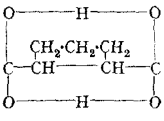


For a constant value of r, the ratio K_1/K_2 should increase with temperature. This increase is observed for all the acids studied, except those having *cis*-structures. That K_1/K_2 decreases with temperature for *cis*-caronic, ββ-dimethylglutaric, and *cyclo*hexane-1 : 1-diacetic acids may indicate that r is increasing with temperature, but an alternative view is that single co-ordination occurs between the carboxyl groups. Such co-ordination of one carbonyl oxygen, causing electron-recession from the hydroxyl oxygen in the same carboxyl group, facilitates ionisation and gives an enhanced value of K_1. The marked decrease in the primary ionisation constants of these *cis*-acids with increase of temperature ($K_1^{25°}$ is approximately twice $K_1^{74°}$) is in harmony with this view, the co-ordination diminishing.

The primary ionisation constants of caronic acid are here compared with those of *cyclo*propane-1 : 2-dicarboxylic acid and its two higher homologues :

Acid.	$K_1 \times 10^5$. *cis.*	*trans.*	References.
Caronic	459	15·2	
*cyclo*Propane-1 : 2-dicarboxylic	46·8	22·4	Wassermann, *Helv. Chim. Acta*, 1930, **13**, 223.
*cyclo*Butane-1 : 2-dicarboxylic	12·6	16·2	Bode, *Ber.*, 1934, **67**, 332.
	6·3	17·0	Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, **11**, 600.
*cyclo*Pentane-1 : 2-dicarboxylic	3·7	11·0	Ingold and Mohrhenn, J., 1935, 949.

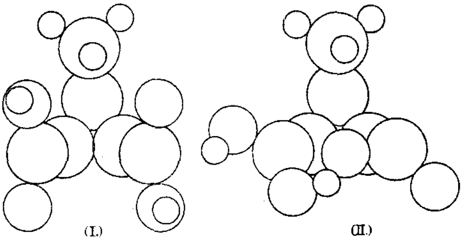
The large value for the primary ionisation constant of *cis*-caronic acid cannot be attributed to the *gem*-dimethyl grouping, for the constant of the *trans*-acid is similar in magnitude to that of *trans-cyclo*propane-1 : 2-dicarboxylic acid. The fact that K_1 for the *cis-cyclo*-pentane- and -*cyclo*butane-1 : 2-dicarboxylic acids is, in each case, less than K_1 for the corresponding *trans*-acids, in spite of the greater proximity of the carboxyl groups, may possibly be due to a double co-ordination of the hydrogens of the carboxyl groups with the carbonyl oxygens of the opposite carboxyl group (see inset). For the pentane acid the distance between the centres of the oxygen atoms of the two carboxyl groups when these are mutually symmetrical is 3·04 Å., or, if the radius of an oxygen atom is taken as 0·60 Å., the net distance between the oxygen atoms is 1·84 Å. The same type of co-ordination may hold to a less extent for *cis-cyclo*butane-1 : 2-dicarboxylic acid. The ratio K_1^{cis}/K_1^{trans} is larger for the butane than for the pentane acids. Calculation, using the valency deflexion theory, shows that the net distance between the oxygen atoms in the undistorted molecule has increased to 2·07 Å. In *cis-cyclo*propane-1 : 2-dicarboxylic acid, the net distance between the oxygen atoms of the two groups has further increased to 2·35 Å., *i.e.*, 0·51 Å. greater than for the *cis-cyclo*pentane acid, and here K_1^{cis} is greater than K_1^{trans}, indicating that such double co-ordination may not now be possible. In *cis*-caronic acid, interference between the *gem*-dimethyl group and the carboxyl groups renders the symmetrical position (I) (Fig. 2) unlikely and favours position (II). If single co-ordination occurs to an appreciable extent, and the model shows that no strain would be involved, augmentation of K_1 would result.



The value of r calculated for *trans*-caronic acid is approximately the same as that for

succinic acid, confirming the extended structure for succinic acid. The percentage decrease in *r* over the temperature range 25—74° is slightly less for *trans*-caronic than for succinic acid, though both appear to be rigid. The substitution of a β-methyl group decreases *r* from 7·18 to 6·38 Å. (cf. Ingold and Mohrhenn, *loc. cit.*), and substitution of a β-*iso*propyl group changes it to 5·95 Å. The structure of glutaric acid is still extended, even when the bulky *iso*propyl group is present, until two β-substituents have been introduced. This change in configuration, associated with the introduction of a second β-substituent, may be connected with the parachors of the methyl esters of the glutaric acids (Vogel, J., 1934, 1758): for the esters of the unsubstituted, the methyl, and the dimethyl acid the parachors are 361·4, 399·9, and 431·8 respectively; the first increment (38·5) is nearly normal for a CH_2 group (39·0), but the second (31·9) is only explicable if the effective volume of the molecule has been diminished by a change in configuration.

FIG. 2.



(I.) (II.)

The lengthening of the hydrocarbon chain from succinic to glutaric acid appears to be attended by an increase in thermal pliability, the percentage decrease in *r* over the temperature range 25—74° being 4·0% for succinic and 6·8% for glutaric acid. For adipic acid the corresponding value is 4·7%. This may possibly be connected with the fact that for the extended chains there is an alternating effect in the orieutation and therefore in the mutual repulsion of the terminal carboxyl groups, which would lead to a greater rigidity of the even members of the series. The greater pliability of adipic acid when loaded with two phenyl groups is marked, the decrease in *r* over the same range being 16·0%. This pliability of the molecule is in harmony with the known formation of chrysene derivatives on ring closure (Ramage and Robinson, J., 1933, 607).

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UNIVERSITY COLLEGE OF N. WALES, BANGOR. [*Received, November 15th*, 1935.]

29. *The Determination of the Melting Points of Organic Substances.*

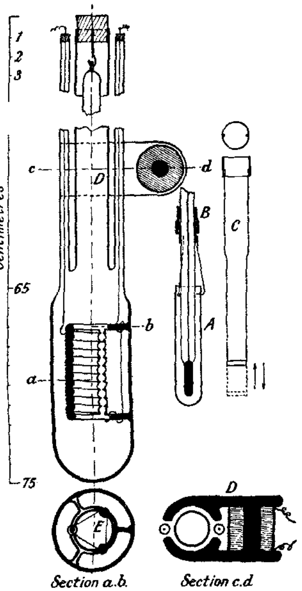
By FRANCIS FRANCIS and F. J. E. COLLINS.

IN investigations in organic chemistry, ***melting points*** are usually determined by the capillary-tube method, and *setting points* by means of a thermometer immersed in the melt. In our experience, a single observer can determine a melting point to within 0·1—0·2°, but the results of different observers, using the same apparatus and the same specimen, may differ by 0·2—0·3°. On the other hand, determinations of the setting point by different observers agree to within 0·02°. Although the melting point and the setting point should be identical for a pure substance, the former is invariably higher than the latter.

During our study of the *X*-ray crystal spacings of the higher *n*-fatty acids and their

derivatives, numerous very pure specimens of these compounds were prepared (Francis, Piper, and Malkin, *Proc. Roy. Soc.*, 1930, *A*, **128**, 214), and it has been found that, when melting or setting points of a homologous series of compounds are plotted against carbon content, graphs are obtained which are only slightly curved. It is therefore possible to check the accuracy of these constants, and a critical study was made of methods of determining melting and setting points. For this purpose we designed a melting-point apparatus by means of which different observers can obtain results which do not differ by more than 0·03°; in addition, it has proved of value in observing certain phenomena which occur in the neighbourhood of the melting point.

FIG. 1.



EXPERIMENTAL.

I. *Setting Points.*—(i) It is usual to take considerable amounts of material for the determination of setting points (*e.g.*, Landolt, *Z. physikal. Chem.*, 1889, **4**, 349, recommends 20 g.), but with a pure or nearly pure material, different observers can obtain results to within ± 0·02° by melting 2—3 g. of the material in a small test tube and stirring it, during solidification, with a thermometer on which 4·6 mm. of scale length is equivalent to 1°.

(ii) With mixtures such as palmitic and stearic acids, much larger quantities of material are necessary; *e.g.*, de Visser (*Rec. trav. chim.*, 1898, **17**, 182) used 50 g. With the apparatus shown in Fig. 1, however, only 2 g. are needed, and different observers can obtain results agreeing to within 0·01°.

The substance under investigation was placed in the container, tube *A*, hanging from clips soldered to a ring which was attached to the thermometer by a piece of rubber tubing at *B*. The stirrer *C* was of platinum, soldered to a ring of soft iron, and operated by the electromagnet *D*. The assembled thermometer, stirrer, and containing tube were placed inside the apparatus shown on the left-hand side, and suspended from a hook at the top, so that the containing tube came within the heating coil, *E*. The whole apparatus was then placed inside a thermostat 70 cm. deep, and 20 × 20 cm. in cross-section, with plate-glass front and back and with a plate-glass vertical part in it, extending to within 5 cm. of the top and bottom to screen the effect in operating a helical stirrer. The temperature in the thermostat was maintained at 0·5° below the setting point of the substance in the containing tube *A*, as determined by the method given in section (i) above. The substance was then heated by means of the coil to 1—2° above its m. p., and readings taken every ½ minute as it cooled. The results were plotted against time, and at the setting point the graph became horizontal, remaining so in the case of a pure substance for 30 minutes or more. The thermometer (8 mm. of stem length = 1°) was calibrated for total immersion at the temperature of observation, and no stem correction was necessary.

In this apparatus, there is no difficulty in obtaining values which agree to ± 0·01°, and with the small amounts of the palmitic and stearic acid mixtures we employed, our results for a series of mixtures agree remarkably with those of de Visser (*loc. cit.*); these will be published later.

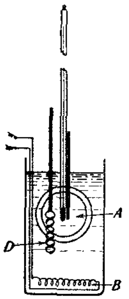
The setting point of pure naphthalene (made for calorimetric work) by the method of section (i) was 80·10° ± 0·02°, and by that just described 80·09° ± 0·01° (Landolt, *loc. cit.*, gives 80·028° ± 0·016°). Our own highly purified specimen of palmitic acid had s. p. 62·53° ± 0·01°, and stearic

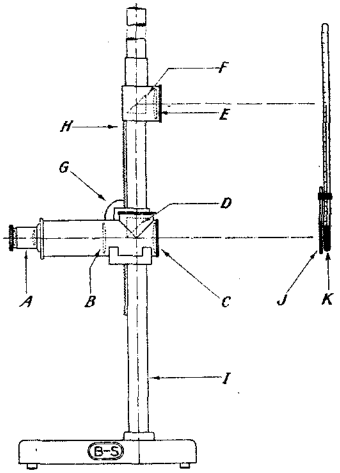
acid, s. p. 69·35° ± 0·01°; these values are very close to those of de Visser and are the highest recorded for these acids.

II. *Determination of Melting Points by the Capillary-tube Method.*—Tseng (*J. Chinese Chem. Soc.*, 1933, **1**, 143; *Sci. Quart., Nat. Univ. Peking*, 1934, **4**, 237, 283) has studied the determination of m. p.'s by the capillary-tube method, and states that, when different types of apparatus are used, discrepancies ranging from a fraction of a degree up to more than 2° are observed. He points out, further, that in the same apparatus individual determinations agree closely and often coincide, although with different observers the divergence may reach 1°. We seldom differed from each other, however, by more than 0·2° in the determination of m. p.'s in the ordinary apparatus, with a bath of sulphuric acid, controlling the temperature by means of a Bunsen flame, and using a thermometer on which 1 mm. of scale length was equivalent to 1°. When

FIG. 3.

FIG. 2.





thermometers with more open scales are used, the temperature of the bath must be controlled much more accurately than is possible with a Bunsen flame, and efficient stirring becomes essential. Further, it is necessary for the observer to watch the material in the capillary tube and the thread of the thermometer through the same eyepiece, and thus to obviate the alternate observation of mercury column and capillary tube, which is necessary in all the ordinary forms of m. p. apparatus.

The bath finally devised is made of cylindrical glass, 9 cm. deep by 5 cm. diameter, into the side of which is fused a small plate-glass window, *A*, through which the capillary tube and its contents can be seen (Fig. 2). The vessel contains heavy liquid paraffin and is heated by a spiral of resistance wire, *B*, immersed at the bottom. The current, and hence the temperature of the bath, is regulated by a rheostat with a lead-screw adjustment. The paraffin is stirred by a small metal stirrer, *D*, driven through a straight shaft coupled to a split-phase A.C. motor. It was essential that this stirrer should run at a constant speed in order to maintain a steady temperature. The thermometer was graduated in 0·1°, 4·6 mm. of scale length corresponding to 1°. It was calibrated by immersion to 2·5 cm., and is supported in the bath to this depth by a rigid iron rod, and a small clip at the side holds the capillary tube close to the bulb of the

thermometer. The temperature of the bath can be maintained to within about ± 0·02° for a period sufficiently long for the determination.

The capillary and its contents *J* (Fig. 3) are viewed by a telescope which incorporates a periscope device, *E*, *F*, so that in the same eyepiece *A* (magnification = 6) both capillary *J* and thermometer scale *K* can be seen together.* A rack-and-pinion adjustment *GH* brings under observation any desired portion of the thermometer scale. Small 12-volt lamps, suitably screened, illuminate both capillary and scale, and are so arranged that the contents of the tube can be viewed by either reflected or transmitted light, or by both simultaneously.

The approximate m. p. is first determined by raising the temperature rapidly, the material is then allowed to resolidify, and the accurate value obtained by raising the temperature to 1° below that point and then at the rate of about 0·1° in 4 minutes, until a clear liquid first appears on the surface of the solid. Under these conditions, different observers do not differ in their readings of the m. p. by more than ± 0·03°.

On slowly raising the temperature of a pure substance which has been previously melted in a capillary tube, a point is reached where a liquid appears over the surface of the solid, and if the temperature is maintained at this point, the whole contents of the tube ultimately liquefy. It is for this reason that the temperature at which the liquid first appears is taken as the m. p. With such substances, there is no " fusion range " or " fusion interval," often mentioned by many and inferentially by those who record a lower and an upper limit when recording m. p.'s. We consider that a " fusion range " is due to impurity of the specimen, or to the formation of metastable forms, or to the fact that the bath has not been maintained at a constant temperature for a sufficient period after the first appearance of the liquid phase. For instance, with mixtures of stearic and palmitic acids containing 47·5 mols. % of the former, the fusion range is 0·35°; this rises with increasing amounts of stearic acid, being 1·3° with 57·5 mols. %, and then falls until with 98·8 mols. % it is 0·1°.

III. *Size of Capillary Tube.*—The most suitable capillary-tube diameter is 1 mm., and all observations should be made on specimens of the material which have been previously melted in it. We have been unable to confirm Landolt's observation (*loc. cit.*) that the m. p. depends on the diameter of the capillary; he found that naphthalene had m. p.'s lying between 79·83° and 80·62° according to the diameter of the tube, but in capillaries of diameters 0·5—3 mm. we always obtained the same value, *viz.*, 80·3°, for the pure hydrocarbon.

IV. *Comparison of Melting Points in Different Forms of Apparatus.*—Melting points taken in the apparatus just described are generally lower than those determined in the usual form. The following comparison was made with nine aliphatic acids and alcohols. The four acids had been described in a previous communication (*loc. cit.*), and the present observations were made in the new form of apparatus and on the same specimens. Our synthetic specimens of the five alcohols were compared with the values given by Piper, Chibnall, and Williams (*Biochem. J.*, 1934, **28**, 2175) for their preparations. In several cases, these authors give a range between which the substances melted, and for the reason previously mentioned, the comparison was made taking the lower temperature as the correct m.p.

Of the nine snbstances, eight gave m. p.'s in our apparatus which were 0·2—0·6° lower than the values with which they were compared, and only one was higher (by 0·2°). One of the most interesting of the former group is hexacosanoic acid, the same specimen of which had m. p.'s 88·2° and 87·7° in the old and the new apparatus respectively, thus confirming our opinion that the old value was too high. Francis, Piper, and Malkin (*loc. cit.*, p. 217) had given the m. p.'s of palmitic and stearic acids as 63·1° and 70·1° respectively; we now find with the same specimens the values 62·85° and 69·9°.

V. *Resolidification Temperature.*—After the m. p. of a substance has been taken, provided no metastable phase be formed, and whilst there is still some unmelted solid in the capillary, if the temperature is allowed to *fall very slowly*, the " resolidification point " can be determined as accurately as the m. p. itself; this point lies closer to the setting point, *i.e.*, the true m. p. of the substance, than does the m. p. determined in a capillary tube. From the table it will be seen that the resolidification temperature is lower than the m. p.—in two cases out of twelve by 0·6°, and in the others by about 0·4° or less. In our experience, a greater difference than 0·6° is an indication of the presence of impurities. Thus the difference between the m. p. of pure palmitic acid and the resolidification point of this acid containing 1% of stearic acid is 0·8°; and in the case of pure stearic acid and the acid containing 1% of palmitic acid, the difference is 1·2°.

* This apparatus was made for us by Messrs. Bellingham and Stanley, 71 Hornsey Rise, N. 19.

The resolidification temperature never differs from the setting point by more than ± 0·2° (see table, col. 6).

Substance.		S. p.	Capillary tube. M. p.	R. p.	Differences. M. p.—S. p.	S. p.—R. p.
n-Fatty acids; C content	16	62·53°	62·85°	62·4°	0·32°	— 0·1°
	18	69·35	69·9	69·3	0·55	0·0
	24	83·9	84·15	83·8	0·25	— 0·1
	26	87·4	87·7	87·2	0·3	— 0·2
Ethyl esters of *n*-fatty acids; C content of acid	26*	59·6	59·95	59·5	0·35	— 0·1
	28	64·2	64·6	64·3	0·4	0·1
	30	68·3	68·45	68·3	0·15	0·0
	34	75·29	75·4	75·3	0·1	0·0
	36	78·3	78·6	78·3	0·3	0·0
Diphenyl †		68·8	69·3	68·7	0·5	— 0·1
Naphthalene †		80·1	80·3	79·9	0·2	— 0·2
Phenyl salicylate †		41·2	41·7	41·3	0·5	0·1

* Metastable modification. † Commercial preparations.

VI. *Effects of Small Amounts of Impurities on the Melting Point.*—Addition of 1% of palmitic or stearic acid to the other acid resulted in definite depressions of m. p.—for palmitic acid from 62·85° to 62·6°, and for stearic acid from 69·9° to 69·3°—but at about 0·1° below these temperatures, the material in the capillary tubes softened. There is also in both cases a small fusion interval of *ca.* 0·1°. These phenomena cover a range of temperature that could only be observed with difficulty in the ordinary form of m. p. apparatus. For reasons which will be discussed in a later communication, it should be stated that both acids were free from traces of oleic acid, which is only removed with difficulty.

VII. *Comparison of Melting Points (Capillary-tube) with Setting Points.*—It is generally recognised that m. p.'s determined by the capillary-tube method are higher than the setting point, but apart from papers by Landolt (*loc. cit.*) and Reissert (*Ber.*, 1890, **23**, 2239), there appear to be no data available as to these differences.

In making the comparisons between "melting," "resolidification," and "setting" points (m. p., r. p., and s. p., respectively) given in the table, we used the same thermometer for each class of determination. Setting points were determined by the method described in Section I, (i), which is sufficiently accurate for this purpose. It will be seen (col. 5) that in every case the difference between the m. p. and the s. p. lies between 0·1° and 0·55°. This may be compared with the corresponding data for the aliphatic acids (Francis, Piper, and Malkin, *loc. cit.*, p. 217) for which the m. p.'s were determined in the usual form of apparatus; in four cases the difference was 0·3° or less, whereas in the other seven it lay between 0·8° and 1·2°. It is clear that in the new form of apparatus the divergence between the m. p.'s taken by the two methods is reduced, but it is nevertheless real. The differences between the resolidification temperature and the setting point, however, are considerably less: in the 12 valnes given in col. 6, four are identical, six differ by 0·1°, and two by 0·2°.

Reissert (*loc. cit.*), in a series of comparisons with substances of m. p. < 115°, found that the differences between m. p. and s. p. were occasionally negative and varied from —0·3° to +0·75°, but it is clear that in some cases his materials were not pure. We have had little experience with substances melting much above 100°. There is, however, no doubt that the divergence at high temperatures would be larger than those given above; *e.g.*, Landolt fonnd that it was 1·8° in the case of mannitol (s. p. 165·64°), and about the same in anthracene (s. p. 200·61°).

The apparatus described above has been of great assistance in observing transition temperatures, particularly in cases such as that of hentriacontane where one is situated 0·2° below the m. p., or in determining the m. p.'s of the α- and the β-modification of ethyl behenate, which differ by 0·45°, or of the two ethyl tetracosanoates which differ by 0·42°. For instance, a specimen of ethyl behenate which has remained for some hours at room temperature in the capillary shows m. p. 48·7°; if the specimen is completely melted, the second α-form separates in the solid phase on cooling, and if a redetermination of the m. p. is made immediately, this form is found to fuse at 48·25°. In the ordinary m. p. apparatus, this phenomenon may be easily overlooked; *e. g.*, Francis, Piper, and Malkin (*loc. cit.*) gave the m. p. as 48·0°, and Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 905) gave it as 48·5—49·5°.

With some long-chain carbon compounds, a marked alteration takes place in the appearance of the solid in the capillary about 0·3° before the m. p. is reached. Substances may lose their crystalline appearance and pass into semi-translucent solids—possibly liquid crystals—or into an apparently amorphous opaque mass (cf. Malkin, J., 1931, 2800).

On the other hand, in the series of the higher aliphatic alcohols synthesised during the course of our work, and in no other derivatives, we noticed in the molten specimens of all those having a carbon content of more than 26 a marked opalescence, which disappeared when the temperature was raised about 0·3° above their m. p.'s. This was also observed in specimens sent to us by Professor Chibnall, and again we consider that this may be due, not to the presence of impurities, but to the formation of liquid crystals. These phenomena can be easily observed, and the temperatures recorded at which they take place, but they have not been further investigated. They may be correlated with transition temperatures, and with the changes observed in the heats of crystallisation and in the dipole moments, which occur at temperatures near the m. p.

SUMMARY.

The *setting point* is the only accurate experimental value for the transition temperature from solid to liquid. When a melting point is determined by the capillary-tube method, higher values are invariably obtained.

The divergence usually observed between the setting point and the melting point is reduced when the latter is determined in the apparatus described in this communication.

The setting point, however, lies nearer to the temperature at which the molten material, allowed to cool very slowly, commences to solidify in the capillary tube. Hence this *temperature affords a better value for the true melting point of a substance than the criterion* used at present.

The apparatus renders it possible to keep the substance under close observation at temperatures near the melting point. Under these conditions, the existence of metastable forms fusing within 1° of each other can be detected, transition temperatures recorded, and a judgment reached on the purity of the specimen.

One of us (F. J. E. C.) thanks the University Colston Society for the award of the Mardon Fellowship, which enabled him to take part in this investigation.

UNIVERSITY OF BRISTOL. [*Received, October 29th*, 1935.]

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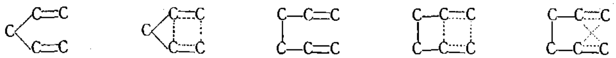
30. *On the Possibility of Ring-chain Mesomerism. Part II. Properties of $\Delta^{\alpha\epsilon}$-Hexadiene-$\alpha\alpha\gamma\gamma\delta\delta\zeta\zeta$-octacarboxylic Esters.*

By CHRISTOPHER K. INGOLD, MUKUNDRAI M. PAREKH, and CHARLES W. SHOPPEE.

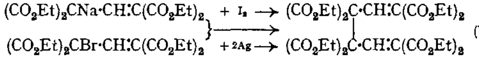
THIS paper records a continuation of our investigation into the evidence of intramolecular interaction between olefinic residues which are separated more widely than in an ordinary conjugated system. The simplest of the systems we have hitherto contemplated contains the form (I), and in the previous part (J., 1928, 365) we reported an examination of certain compounds of this type. These were derivatives of phorone. It was shown that whilst some, including phorone itself, have all the physical and chemical characteristics of open-chain diolefins, others undoubtedly possess an isomeric ring structure, and yet others display a character which makes it difficult to decide to which class they belong. The last exhibit physical and chemical properties indicating greatly reduced unsaturation, and they show on the one hand a propensity for giving substitution products which are undeniable ring compounds, and on the other a capacity for yielding the derivatives to be expected from an open-chain structure. These properties suggest a form of "conjugation" implying interaction at both ends of the olefinic residues, and we expressed this conclusion

in a symbol (II), which is to be interpreted as signifying an appreciable probability of electron exchange along each of the tracks indicated. We observed that the effect described became marked only in the presence of substituents which should polarise the double bonds in a way calculated to cause them to attract each other.*



(I.) (II.) (III.) (IV.) (V.)

We then turned to the consideration of the case in which two saturated carbon atoms separate the olefinic residues (III). The possible types of interaction are shown in formulæ (IV) and (V), and that represented by the latter formula seemed likely to be the easier to realise, since this formula contains only one four-membered quasi-ring, whereas the other contains two. We therefore planned to create the form of polarisation which should favour this mode of interaction by attaching electron-attracting groups to the ends of the six-carbon chain; and, as a practical step, we decided to investigate the properties of the compound which should be obtained by the action of iodine on ethyl sodiodicarboxyglutaconate. Then we found that Guthzeit and Hartmann had already carried out this condensation (*J. pr. Chem.*, 1910, **81**, 329), and on account of the unexpected properties of the product had reached some remarkable conclusions concerning its constitution:



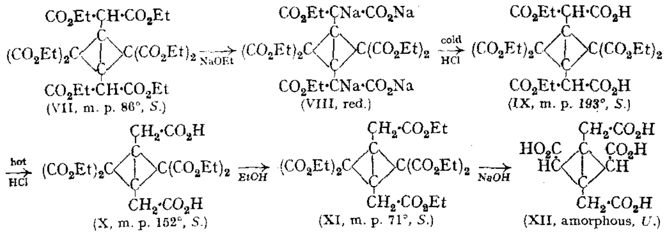
(VI.)

The product which should be (VI), a crystalline ester (m. p. 86°), may be obtained not only in the manner stated but also by several allied methods, including the action of silver on ethyl α-bromodicarboxyglutaconate (Ingold and Shoppee, J., 1930, 1619), and the action of the bromo-compound on the sodio-compound. All these methods point to structure (VI). However, as Guthzeit and Hartmann first observed, the substance is completely saturated to permanganate, chlorine, and bromine. These authors therefore rejected formula (VI) and regarded the substance as dicyclic. Their particular dicyclic formula (VII) involves a *bicyclo*butane nucleus, and they arrived at it on the basis of data and reasoning which it is necessary to summarise.

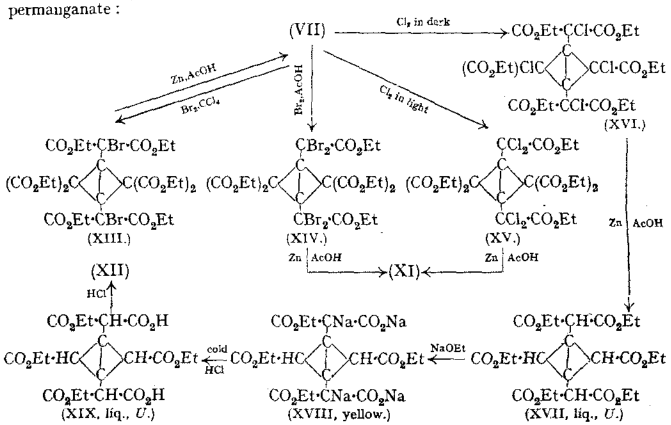
The data relate to three groups of reactions, of which we may first consider hydrolysis. On dissolution in cold sodium ethoxide the octa-ester, m. p. 86°, gave a red tetrasodium salt (VIII), which on acidification yielded a hexa-ester di-acid, m. p. 193° (IX), reconvertible into the octa-ester. Any of these compounds on hydrolysis with acids gave a tetra-ester di-acid, m. p. 152° (X), convertible by esterification into a hexa-ester, m. p. 71° (XI). The compounds (VII), (IX), (X), and (XI) were stable towards permanganate. Any of them on alkaline hydrolysis yielded an amorphous tetra-acid (XII), which, like its liquid

* As Part I was published in 1928, it seems desirable to indicate the changes of theory and nomenclature which have taken place in the meantime. Employing the general conception then called "electronic strain," Ingold and Shoppee (*loc. cit.*, pp. 384—5) advocated the idea of a molecular state intermediate between those for which ordinary formulæ could be written—in contradistinction, for instance, to Sugden's suggestion (*ibid.*, p. 412) that separate isomerides corresponding to the ordinary formulæ were present in equilibrium. To Ingold and Shoppee's original view we still adhere. However, it was not until 1929 that the physical mechanism involved in the production of such an intermediate state was perceived by Burton and Ingold as an extrapolation of the exchange theory of the localised bond and therefore as a factor of molecular stability; thus no description of the intermediate state in terms of electron exchange or hybridised wave functions will be found in Part I. The difficulty of nomenclature, which incongruously led in 1928 to the use of the term "valency tautomerism" for something which was carefully explained to be nothing to do with tautomerides, was not cleared up until, in 1933, the word "mesomerism" was introduced, which is now used in the serial title (cf. *Proc. Leeds Phil. Soc.*, 1929, **1**, 421; J., 1933, 1120; *Nature*, 1934, **133**, 946).

methyl and ethyl esters, was instantly oxidised by permanganate. In the following formulæ *S* signifies stable and *U* unstable towards permanganate :

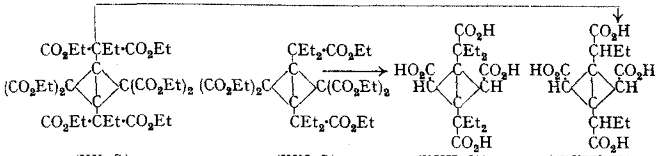


The second group of experiments relates to halogenation, which in every case is represented as a substitution process. Bromination of the octa-ester (VII) in carbon tetrachloride solution gave a dibromo-octa-ester (XIII), reducible by means of zinc and acetic acid to the original compound. Further bromination in acetic acid yielded a tetrabromo-hexa-ester (XIV), which on reduction with zinc and acetic acid gave the hexa-ester of m. p. 71° (XI). Chlorination in sunlight yielded a tetrachloro-hexa-ester (XV), which likewise on reduction gave the hexa-ester, m. p. 71°. On the other hand, chlorination in the dark produced an isomeric tetrachloro-hexa-ester (XVI), which was reduced by zinc and acetic acid to a liquid hexa-ester (XVII). This when treated with cold sodium ethoxide gave a yellow tetrasodium compound (XVIII), from which acids liberated a liquid tetra-ester di-acid (XIX), readily hydrolysable by means of acids to the amorphous tetra-acid (XII). The hexa-ester (XVII) and all compounds derived from it were instantly oxidised by permanganate :



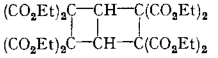
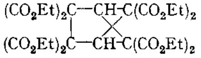
The third series of observations relates to alkylation, which is stated to have been effected by the use of zinc and ethyl iodide. The product was a mixture of a diethylated octa-ester (XX) and a tetra-ethylated hexa-ester (XXI). These compounds were not

attacked by permanganate. By hydrolysis they were converted into the diethylated tetra-acid (XXIII) and the tetra-ethylated tetra-acid (XXII) respectively. These mixed acids, and likewise their esters, were instantly oxidised by permanganate.



(XX, *S.*) (XXI, *S.*) (XXII, *U.*) (XXIII, *U.*)

These results and interpretations are those given by Guthzeit and Hartmann, and the general nature of their reasoning is as follows. As stated above, the necessity for some form of saturated dicyclic structure is assumed on account of the saturated nature of many of the substances. Three sets of observations, *viz.*, the formation of the coloured tetra-sodium salts, the course of the halogenation, and of the alkylation, all show that the original octa-ester contains two residues $-CH(CO_2Et)_2$, each with replaceable hydrogen. This consideration rules out dicyclic formulæ such as (XXIV) and (XXV). Indeed it rules out all structural conceptions which require more than four carbon atoms for the construction of the dicyclic nucleus. Thus Guthzeit and Hartmann's formula is unequivocally indicated, and support for it is obtained from the circumstance that, when the scheme of inter-relations is worked out as shown above, a definite regularity is seen in the peculiar division of the compounds into those which are stable towards permanganate and those which are attacked (cf. the symbols *S* and *U*). The labile compounds are just those which have hydrogen directly linked to the C_4-nucleus. The assumption can therefore be made that hydrogen thus situated provides a necessary point of attack for the oxidising agent.

(XXIV.)   (XXV.)

Dissatisfied with this interpretation but perceiving no flaw (except, of course, that the modes of formation of the octa-ester are unexplained), we commenced a repetition of the work, and also an examination of the corresponding methyl esters with a view to obtaining crystalline analogues of some of the substances which Guthzeit and Hartmann describe as liquids. The two investigations did not run entirely parallel, and we may describe our results for the ethyl series first, as they differ in many important respects from those recorded by Guthzeit and Hartmann. Our findings are as follows.

The octa-ester, m. p. 86°, is formed as Guthzeit and Hartmann describe; towards permanganate it has all the stability they attribute to it, and towards halogens more (see below).

The red tetrasodium salt of Guthzeit and Hartmann does not exist. It is possible by the action of sodium ethoxide to obtain a small quantity of an apparently red solid, but the colour is in the mother-liquor, and the solid does not contain half of the amount of sodium required by formula (VIII). The probable nature of this material is indicated by our work in the methyl ester series (see below).

The hexa-ester di-acid, m. p. 193°, can be obtained by acidification of a mixture of the octa-ester and alcoholic sodium ethoxide, but not by way of the solid compound as Guthzeit and Hartmann claim. It has the stability ascribed to it, and is a partial hydrolysis product of the octa-ester, into which it can be reconverted by esterification.

The tetra-ester di-acid, m. p. 152°, and the hexa-ester, m. p. 71°, both exist, but the empirical formulæ ascribed to them by Guthzeit and Hartmann are incorrect. Each has one molecule of water of constitution more than is represented in formulæ (X) and (XI). Guthzeit and Hartmann describe the acid as crystallising with $1H_2O$ or $3H_2O$. We could

not prepare their trihydrate. The water of their monohydrate, however, cannot be removed from the acid. Furthermore, it is present in, and cannot be removed from, the dianilide. It is present also in the hexa-ethyl ester, even after distillation. The anhydrous salts and ester of Guthzeit and Hartmann's description have no real existence. Both the acid and the neutral ester are stable towards permanganate, and we have shown them to contain an alcoholic hydroxyl group.

The composition of the tetrabasic acid (which when pure has m. p. 193°) is also incorrectly given by Guthzeit and Hartmann, and so are those of its methyl and ethyl esters. Actually all these compounds contain an additional molecule of water of constitution. Guthzeit and Hartmann describe them all as causing instantaneous reduction of permanganate. We find, on the contrary, that they are stable towards permanganate. We have proved the presence of an alcoholic hydroxyl group.

We were for long completely misled by these numerous errors of composition. Guthzeit and Hartmann's paper records 40 analyses all in very good agreement with incorrect formulæ. Concerning Guthzeit and Hartmann's description of the halogenation and alkylation of the octa-ester, our experience in a prolonged investigation is simply that none of the reported reactions takes place. All these results are confirmed by our work on the methyl esters.

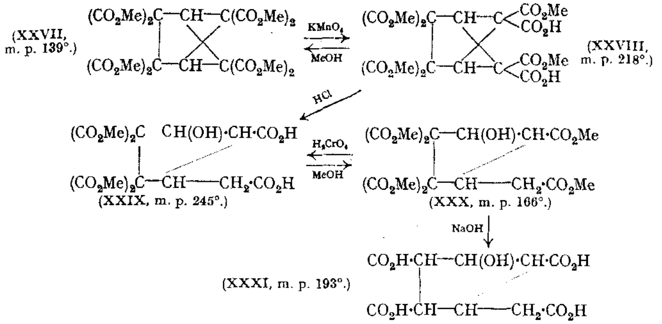
The foregoing observations destroy the foundations of the *bicyclo*butane formula, which is based primarily on the supposed presence in the octa-ester of two readily replaceable hydrogen atoms, and in an auxiliary manner on the alleged separation of derivatives of the octa-ester into the two classes characterised respectively by marked stability and marked instability towards permanganate. However, destruction of support is not proof of falsity, and the work thus far described does not show the *bicyclo*butane structure to be inapplicable to the octa-ester and the hexa-ester di-acid—the two compounds of the series which Guthzeit and Hartmann analysed correctly.

Our remaining evidence is derived from investigations in the series of methyl esters. The *octamethyl* ester, m. p. 139°, was prepared analogously to the ethyl ester. Its composition was normal, and it had the expected great stability towards permanganate. It was, however, broken down by means of ozone, and the products were methyl ethanetetracarboxylate and oxalic acid. Subsequently a similar decomposition of the octa-ethyl ester was observed. This definitely disposes of the *bicyclo*butane structure, and shows that we must interpret the observations on the lines of formulæ such as (VI), (XXIV), and (XXV). For purposes of illustration we shall henceforth employ whichever of these alternatives appears most convenient in the case considered, reserving until later the discussion of apparent inconsistencies:

$$\underset{\text{(XXVI.)}}{\begin{array}{l}(CO_2Me)_2C\cdot CH{:}C(CO_2Me)_2\\ \quad\quad\;\;|\\ (CO_2Me)_2C\cdot CH{:}C(CO_2Me)_2\end{array}} \xrightarrow[2O_3]{} \begin{array}{l}(CO_2Me)_2C\cdot CO_2H\\ \quad\quad\;\;|\\ (CO_2Me)_2C\cdot CO_2H\end{array} + 2CO(CO_2Me)_2 \longrightarrow \begin{array}{l}(CO_2Me)_2CH\\ \quad\quad\;\;|\\ (CO_2Me)_2CH\end{array} + 2(CO_2H)_2$$

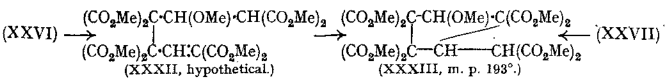
For a reason given below, it was not found possible to convert the octamethyl ester into a ***hexamethyl ester di-acid*** by the action of sodium methoxide. This ester-acid was, however, encountered during attempts to oxidise the octa-ester with alkaline permanganate and ferricyanide. Its composition was normal, and its relation to the octa-ester was confirmed by its reconversion into the latter (XXVII, XXVIII). Hydrolysis of either of these compounds with mineral acids gave the *tetramethyl ester di-acid* (XXIX), which contained the extra molecule of water of constitution, but was saturated towards oxidising agents. It could not be degraded even by means of ozone. The distilled *hexamethyl* ester (XXX), which, like its ethyl analogue, is crystalline, also contained this extra water molecule. It was unattacked by ozone, and attempts to oxidise it by means of hot chromic acid merely gave back the tetramethyl ester di-acid. The presence of an alcoholic hydroxyl group was proved. All four of these esters on hydrolysis with sodium hydroxide gave the tetrabasic acid (XXXI) already described. In formulating these transformations we assume hydrolysis to be initiated in those carbomethoxy-groups which may be presumed

to be the least sterically protected; they are also those most closely associated with the system concerned in addition of water:



(XXVII, m. p. 139°.) (XXVIII, m. p. 218°.) (XXIX, m. p. 245°.) (XXX, m. p. 166°.) (XXXI, m. p. 193°.)

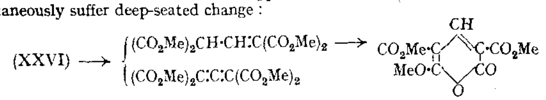
When the octamethyl ester, m. p. 139°, was dissolved in cold alcoholic sodium methoxide, and the solution acidified, the main product was an *ester*, m. p. 193°, having the composition of the original octa-ester plus a molecule of methyl alcohol. This is not solvent of crystallisation, because the compound can be distilled without decomposition; furthermore, the original octa-ester does not in fact take up methyl alcohol when crystallised from this solvent. The addition ester, m. p. 193°, was shown to contain nine methoxyl groups. It was formed very easily, although alkaline conditions appeared to be necessary: we obtained it from the octa-ester of m. p. 139°, not only as already described, but also by the action of cold methyl-alcoholic potassium hydroxide, and even methyl-alcoholic potassium cyanide, but we did not encounter it when esterifying the acid-ester of m. p. 218° with methyl alcohol and hydrogen chloride. It is probable that the sodium salt encountered in the experiments upon the ester ethyl is formed in a similar reaction, which, however, is overlaid in this case by much more rapid and extensive partial hydrolysis. The circumstance that addition of alcohol and hydrolysis were not observed to occur in the same molecule may be taken as an indication that the two processes are located in the same part of the molecular system. Two modes of formation of the addition ester, m. p. 193°, to which we ascribe formula (XXXIII), are represented below; one of them involves a hypothetical intermediate (XXXII):



(XXXII, hypothetical.) (XXXIII, m. p. 193°.)

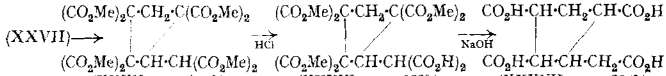
As contrast to what follows it is worth noting that not only this methoxy-ester, but all the neutral esters mentioned in this paper which have an extra molecule of water or alcohol of constitution, can be distilled without decomposition. Ingold and Shoppee have already recorded the decomposition by distillation of the octa-ethyl ester (m. p. 86°) (*loc. cit.*), but the observation was published for a reason which had nothing to do with the object of this paper, and its constitutional significance was not discussed. We now report the corresponding experiment with the octamethyl ester, m. p. 139°. In each case only half the original molecule appears in recognisable form, and this is a pyrone (*e.g.*, XXXIV). Its constitution reveals one of the two double links that can be ascribed to the original structure, and shows that a fission has occurred at the $\gamma\gamma'$-link which the ozonolytic experiment proved to be present. The pyrolysis may be illustrated as follows; it is known that the methyl dicarboxyglutaconate postulated as an intermediate would, if formed, undergo

the reaction assumed, and it is supposed that allenetetracarboxylic ester would simultaneously suffer deep-seated change :



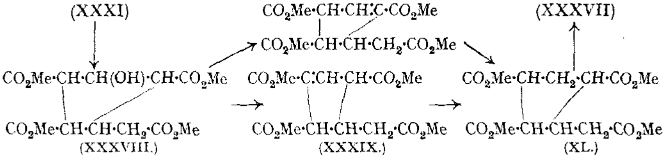
(XXXIV.)

Although the octamethyl ester could not be reduced by zinc and acetic acid, nor yet by hydrogen at a platinum or palladium catalyst, it was successfully hydrogenated in acid solution by an electrolytic method. The product was a *dihydro-octa-ester*, m. p. 149°, which could be distilled without decomposition and appeared to be saturated. It was stable towards permanganate, and could not be further reduced by prolonged renewal of the treatment under which it was formed. On account of these properties we ascribe to it formula (XXXV). It was hydrolysed by means of hydrochloric acid to the *hexa-ester di-acid* (XXXVI), which in turn was completely hydrolysed by sodium hydroxide to the tetrabasic acid (XXXVII) :



(XXXV, m. p. 148°.) (XXXVI, m. p. 252°.) (XXXVII, m. p. 225°.)

We tried to prepare this acid from the hydroxy-tetrabasic acid (XXXI) by successive esterification, dehydration, hydrogenation and hydrolysis :



(XXXVIII.) (XXXIX.) (XL.)

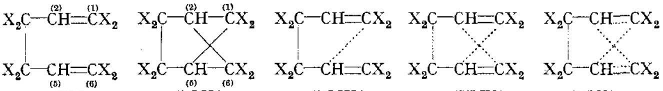
These reactions were realised : dehydration of the hydroxy-ester (XXXVIII) was effected by means of potassium hydrogen sulphate, and reduction of the unsaturated product by hydrogen in the presence of platinum. However, the final acid, for which there are a number of stereochemical possibilities, was a mixture which could not be separated.

With regard to halogenation and alkylation the methyl esters are in the same case as the ethyl esters. In particular the attack of halogens on the octamethyl ester, m. p. 139°, was very slow even with strong irradiation, and no definite product could be obtained. Alkylation of the octamethyl ester could not be effected either by Guthzeit and Hartmann's method, or by any other that we tried, including even the employment of sodamide.

These are the observations, and it remains now to consider what conclusions may be drawn concerning the structure to be ascribed to the original condensation products, the octa-esters of m. p. 86° and 139°. We have shown above that the types of structure which might possibly be considered in this connexion are confined to three alternatives. One of these, the structure with two fused *cyclo*butane rings, may forthwith be dismissed, as it does not account intelligibly for any of the additive transformations described above: we know that ditertiary alicyclic bonds, CH—CH, are never broken, even in highly strained *cyclo*propane derivatives, by additive reagents such as we have employed.

Decision between the other two structures is extremely difficult ; the situation appears to be as follows. The decomposition with ozone indicates the unsaturated structure (XLI), but the great stability of the compounds to permanganate suggests the dicyclic structure (XLII) : it can be reconciled with formula (XLI) only if we import the supposition that the double bonds suppress each other's reactivity in some way not expressed in the formula

itself. The addition of methyl alcohol under alkaline conditions can be explained by means of either structure. The attack is evidently by the methoxide ion, and, employing the unsaturated structure (XLI), it may be supposed that methyl alcohol adds to one double bond by a process analogous to the Michael reaction, and that then a real Michael reaction closes the *cyclo*pentane ring. The analogy permitting interpretation on the basis of the dicyclic structure (XLII) is the additive fission of suitably carboxylated strained rings by processes similar to the Michael reaction (*e.g.*, addition of ethyl cyanoacetate to ethyl *cyclo*propane-1 : 1-dicarboxylate) : the 1 : 1 : 6 : 6-carboxyl groups in the 1 : 2 : 6 : 5-*cyclo*butane ring are so disposed that an addition product of the correct constitution could be formed in one step. The addition of water in acidic media cannot, however, be interpreted by formula (XLI) on the lines suggested above, because the Michael reaction required to close the ring could not take place under such experimental conditions. The observation of this addition thus indicates formula (XLII); and we know analogies for the acid hydrolytic fission of strained rings where there is a bond rendered electrically dissymmetric by substitution (*e.g.*, conversion of caronic acid into terebic acid). As to the electrolytic reduction in acid solution, the doubly bonded structure (XLI) once again appears inadequate. Certainly it suggests that reduction might occur, but it does not explain why, after two atoms of hydrogen have been taken up, hydrogenation ceases and a ring is formed; furthermore, it does not suggest how such a ring could be produced at that stage of the process under the experimental conditions obtaining. On the other hand, in the dicyclic structure (XLII) a ring has merely to be broken, and the disposition of carboxyl groups in the *cyclo*butane ring should confer on this ring a definite tendency to reductive fission, since the attacks of electrons and of nucleophilic anions (*e.g.*, methoxide) are analogous.



(XLI.) (XLII.) (XLIII.) (XLIV.) (XLV.)

($X = CO_2Me$ or CO_2Et.)

It seems that the only way of forcing an interpretation employing but one of these two formulæ to cover all known circumstances is to import *ad hoc* assumptions extraneous to the normal conceptual content of the formula adopted. We might, for example, adopt formula (XLI), and assume, further, (1) that the double bonds are " 1 : 5-conjugated " in the sense that they allow 2 : 6-addition with 1 : 5-ring closure, which would be the analogue of αδ-addition with βγ-double bond formation in ordinary butadienoid conjugation; and (2) that the two double bonds largely suppress each other's reactivity. The first assumption makes addition and ring closure mutually dependent and simultaneous, and thus it gets over the difficulty that ring closure would not take place as a separate act under the conditions of many of the observations. Formula (XLIII) expresses this idea. It does not, however, adequately represent the stability of the system : it implies reduced reactivity at atoms 1 and 5 but not at atoms 2 and 6, just as the conception of butadienoid conjugation implies suppressed reactivity in the middle of the chain but not at the free ends. For this reason we require the second assumption also; and its introduction amounts to assuming that the " conjugation " is actually cyclic, affecting all the atoms 1, 2, 5, and 6. A confirmatory consideration is that the spatial symmetry of the system would have made it difficult to understand an association between atoms 1 and 5 without a similar association between atoms 2 and 6. The expression for this " conjugation " must therefore be changed to that of formula (XLIV).

It remains to be observed that, whether the properties of these compounds are expressed by the combination of ordinary formulæ (XLI and XLII) or by the single " conjugation " formula (XLIV), the implied physical idea is the same. Thus the physical significance of the " conjugation " formula is that part of the normal electron-content of the two double bonds is forming a charge cloud along the lines which mark the " conjugation ";

or, to put it in another way, electron exchange is permitted in these directions as well as in the bonds. The electron conservation is better brought out by rewriting the "conjugation" formula as in (XLV). With regard to the pair of ordinary formulæ, (XLI) and (XLII), it is obvious that we must combine them as the canonical structures of a system in resonance, and not as independently existing, mutually convertible tautomerides, for our object is to explain a special stability. Their wave functions when mixed must give the wave function of (XLV), and their energies must be replaced by the smaller energy of (XLV). This is just the molecular condition we set out to seek, and although on many occasions the research has seemed to be leading in quite other directions, it appears to us when we review our results that the original object has been achieved.

EXPERIMENTAL.

Methyl and Ethyl $\Delta^{\alpha\epsilon}$*-Hexadiene-ααγγδδζζ-octacarboxylate* [*Methyl and Ethyl* (1 : 1 : 2)-bicyclo*Hexane*-1 : 1 : 3 : 3 : 4 : 4 : 6 : 6-*octacarboxylate*].—For the preparation of the methyl ester the starting points were methyl αα′-dicarboxyglutaconate, m. p. 43° (Found : C, 47·9; H, 5·0. Calc. : C, 48·2; H, 5·1%), its yellow sodio-derivative, m. p. 247—249°, its green copper salt, m. p. 246—248° (decomp.), and its α-bromo-derivative (Found : Br, 22·8. Calc. : Br, 22·7%). The methyl ester named in the heading was prepared from the sodio-compound and iodine, from the bromo-compound and sodium or silver, from the copper compound and sulphur, and from the bromo-compound and the sodium compound, the methods being modelled on those given by Guthzeit and Hartmann or Ingold and Shoppee (*locc. cit.*). Crystallised from acetone, the *octamethyl* ester formed prisms, m. p. 139° (Found : C, 48·4, 48·5, 48·1; H, 4·8, 5·0, 4·8. $C_{22}H_{26}O_{16}$ requires C, 48·4; H, 4·8%). The corresponding octa-ethyl ester is the compound described as having other constitutions by Guthzeit and Hartmann and by Faltis and his collaborators (references, see Ingold and Shoppee). Our preparation had m. p. 86° (Found : C, 54·7; H, 6·45. Calc. : C, 54·7; H, 6·4%).

Hexamethyl Dihydrogen and Hexa-ethyl Dihydrogen $\Delta^{\alpha\epsilon}$*-Hexadiene-ααγγδδζζ-octacarboxylate* [*Hexamethyl Dihydrogen and Hexa-ethyl Dihydrogen* (1 : 1 : 2)-bicyclo*Hexane*-1 : 1 : 3 : 3 : 4 : 4 : 6 : 6-*octacarboxylate*].—The former of these compounds was obtained as the product of an attempted oxidation of the octamethyl ester by the prolonged action of 2·5% permanganate in alkaline aqueous acetone. When worked up in the usual way, the crystalline acid ester separated after most of the acetone had been removed by distillation. The same acid ester was obtained also in the course of an attempted oxidation of the octamethyl ester by means of alkaline ferricyanide. The ester (1 g.) was heated on the steam-bath for 24 hours with a solution of potassium ferricyanide (2·5 g.) and potassium carbonate (0·7 g.) in water (80 c.c.). An ethereal extract of the neutralised solution, and an acetone extract of the precipitate which had been formed, both yielded the acid ester. (The octamethyl ester was, however, recovered unchanged after being boiled for 6 hours with chromic anhydride in glacial acetic acid.) Crystallised from acetone, the acid-ester had m. p. 218° (decomp.), but the product of thermal decomposition was a thick dark oil which could not be crystallised [Found : C, 46·0; H, 4·6; equiv. (titration), 258. $C_{20}H_{22}O_{16}$ (dibasic) requires C, 46·3; H, 4·3%; equiv., 259]. A solution of the acid (2 g.) in methyl alcohol (25 c.c.) was saturated with hydrogen chloride, kept over-night, warmed for a short time, and evaporated. The product was the octamethyl ester, m. p. and mixed m. p. 139°. The hexa-ethyl dihydrogen ester (Guthzeit and Hartmann) had m. p. 193° (decomp.) after crystallisation from ethyl acetate containing ligroin (Found : C, 51·9; H, 5·7; OEt, 44·6. Calc. : C, 51·9; H, 5·7; OEt, 44·8%). The product of its thermal decomposition at 200° was a thick brown oil which could not be crystallised. The acid ester was treated with thionyl chloride on the steam-bath for 2 hours, and the excess of the reagent removed under reduced pressure. Desiccation of the product over potassium hydroxide yielded the crystalline *hexa-ethyl ester dichloride*, $C_6H_2(CO_2Et)_6(COCl)_2$, which after crystallisation from ether–ligroin had m. p. 65—66° (Found : C, 48·9; H, 5·1; Cl, 11·1. $C_{26}H_{32}O_{14}Cl_2$ requires C, 48·8; H, 5·1; Cl, 11·1%). This compound was converted quantitatively into the octa-ethyl ester, m. p. and mixed m. p. 86°, by boiling with dry ethyl alcohol and evaporating the excess of the latter. Esterification of the acid ester, m. p. 193°, was also accomplished through the silver salt, which was soluble in water, and on concentration of its solution separated as a solidifying oil. The solid reacted readily with ethyl iodide, evolving heat and giving the octa-ethyl ester, m. p. and mixed m. p. 86°.

*Tetramethyl Dihydrogen and Tetra-ethyl Dihydrogen 3-Hydroxy-2 : 4 : 4 : 5 : 5-pentacarboxy*cyclo*pentane-1-acetate.*—The former *hydroxy-acid-ester* was prepared from the octamethyl ester

(10 g.) by boiling with 20% hydrochloric acid (100 g.) until solution was almost complete and the evolution of carbon dioxide ceased. The product, which separated in prisms on cooling, was crystallised from acetone. It became discoloured at 235° and had m. p. 245° (decomp.). It was unaffected by boiling with potassium dichromate and dilute sulphuric acid or with concentrated nitric acid, and by treatment in chloroform solution with ozone [Found : C, 45·9; H, 4·8; equiv. (titration), 208·4. $C_{16}H_{20}O_{13}$ (dibasic) requires C, 45·7; H, 4·8%; equiv., 210]. The hexamethyl dihydrogen ester was used in place of the octamethyl ester, and 10% sulphuric acid in place of hydrochloric acid, in the above preparation. In each case a gummy by-product was obtained which could not be purified. The tetra-ethyl hydroxy-acid-ester was prepared but incorrectly formulated by Guthzeit and Hartmann, whose trihydrate we could not obtain. Our preparations, crystallised from ether–ligroin, had m. p. 152°. A sample was analysed after drying in a vacuum over sulphuric acid (Found : C, 50·5; H, 6·0. Calc. for $C_{20}H_{28}O_{13}$: C, 50·4; H, 5·9%). The same material was crystallised from hydrochloric acid and air-dried (Found : C, 50·4; H, 5·9%). By digestion with thionyl chloride for 1 hour on the steam-bath, removal of excess of the reagent by distillation, and treatment of the resulting chloride with aniline, a *dianilide* was obtained, which crystallised from ether–acetone in needles, m. p. 152° (Found : C, 61·1; H, 6·0; N, 4·4. $C_{32}H_{38}O_{11}N_2$ requires C, 61·3; H, 6·1; N, 4·5%).

*Methyl and Ethyl 3-Hydroxy-*2 : 4 : 4 : 5 : 5-*pentacarboxy*cyclo*pentane-*1-*acetate*.—The above tetramethyl dihydrogen ester underwent considerable conversion into the *hexamethyl* ester when the attempt was made to crystallise the former from methyl alcohol. Quantitative conversion was effected by the Fischer–Speier method, or by the use of sulphuric acid as catalyst. The neutral ester separated from methyl alcohol in short needles, m. p. 168°, and could be distilled completely without decomposition at 5 mm. (m. p. again 168°, mixed m. p. the same) [Found (not distilled) : C, 47·9; H, 5·45. Found (distilled) : C, 48·0; H, 5·6. $C_{18}H_{24}O_{13}$ requires C, 48·2; H, 5·4%]. On boiling with potassium dichromate and dilute sulphuric acid the hexamethyl ester was converted into the tetramethyl dihydrogen ester described above. After prolonged treatment with ozone in chloroform it was recovered unchanged. It did not appear to react with acetyl chloride, acetic anhydride, diazomethane or thionyl chloride, but Tschugaeff and Zerewitinoff's reagent yielded approximately the correct amount of methane (Found : OH, 3·6. Calc., 3·8%). The hexa-ethyl ester was prepared by Guthzeit and Hartmann but incorrectly analysed. Our material, obtained by the Fischer–Speier method, separated from ethyl acetate–ligroin in large prisms, m. p. 71°. It was completely distilled without decomposition, b. p. 250°/4 mm., and the distillate had again m. p. 71°, mixed m. p. the same [Found (undistilled) : C, 54·2; H, 6·8. Found (distilled) : C, 54·15; H, 6·8. Calc. for $C_{24}H_{36}O_{13}$: C, 54·1; H, 6·8. Calc. for $C_{24}H_{34}O_{12}$: C, 55·9; H, 6·5%. Guthzeit and Hartmann record C, 55·9; H, 6·5%, and four other closely agreeing analyses]. The ester was unaffected by phosphorus oxychloride, but reacted with phosphorus pentachloride in chloroform : we could not purify the chloro-compound. The hydroxy-ester also responded to the Tschugaeff–Zerewitinoff reagent.

3-*Hydroxy*-2 : 4 : 5-*tricarboxy*cyclo*pentane*-1-*acetate and its Methyl and Ethyl Esters*.—The acid was prepared by boiling either the octamethyl ester, the hexamethyl dihydrogen ester, the acid methyl hydroxy-ester, or the neutral methyl hydroxy-ester, or any of the corresponding ethyl esters with 10% aqueous-alcoholic potassium hydroxide. For example, the hydroxy-ester (10 g.) was boiled for 15 hours with a solution of potassium hydroxide (10 g.) in a mixture of methyl alcohol (34 c.c.) and water (66 c.c.). This acid was prepared by Guthzeit and Hartmann, although it and its silver salt and methyl and ethyl esters were all incorrectly analysed. The product was isolated as its silver salt by Guthzeit and Hartmann's method. The salt, suspended in dry ether, was decomposed by means of hydrogen sulphide, and the acid, part of which was obtained by evaporation of the ether and part by extracting the silver sulphide with ethyl acetate, was crystallised (3 g.) to constant m. p. from ethyl acetate containing acetone. It separated in small rectangular prisms, m. p. 193°. Guthzeit and Hartmann described this acid as amorphous and instantly oxidised by permanganate. The pure acid is stable towards permanganate, and is unaffected either by lead peroxide in glacial acetic acid at 100° or by chromic acid in acetic acid at 30°. It gives a yellow colour with ferric chloride [Found : C, 43·7, 43·8; H, 4·6, 4·7; *M* (Rast), 283, 299. Calc. for $C_{10}H_{12}O_9$: C, 43·5; H, 4·4%; *M*, 276. Calc. for $C_{10}H_{10}O_8$: C, 46·5; H, 3·9%; *M*, 258. Guthzeit and Hartmann record C, 46·4; H, 4·0%, and five other closely agreeing analyses. Found for the Ag salt : C, 16·75, 16·95; H, 1·4, 1·4; Ag, 59·4, 59·5. Calc. for $C_{10}H_8O_9Ag_4$: C, 17·0; H, 1·15; Ag, 61·4%. Calc. for $C_{10}H_6O_8Ag_4$: C, 17·5; H, 0·9; Ag, 62·9%. Guthzeit and Hartmann record C, 17·6; H, 1·0; Ag, 62·8%, and several other analyses closely agreeing]. The methyl ester was obtained from

the silver salt and methyl iodide as a viscous, pale yellow oil, b. p. 205°/3 mm., which did not decolorise permanganate in acetone (Found : C, 50·6; H, 5·9. Calc. for $C_{14}H_{20}O_9$: C, 50·6; H, 6·1%. Calc. for $C_{14}H_{18}O_8$: *C*, 53·5; *H*, 5·8%. *Guthzeit* and Hartmann *record as found* : C, 53·4; H, 5·9%). This compound could not be smoothly acetylated, but it reacted with the Tschugaeff–Zerewitinoff reagent, giving methane, as was proved by analysis of the gas (Found : OH, 4·5. Calc., 5·1%); the dehydration of the hydroxy-ester with potassium hydrogen sulphate is described later. The corresponding ethyl ester, b. p. 200°/about 1 mm., was similarly prepared and had similar properties (Found : C, 55·2; H, 7·35. Calc. for $C_{18}H_{28}O_9$: C, 55·6; H, 7·3%. Calc. for $C_{18}H_{26}O_8$: C, 58·35; H, 7·1%. Guthzeit and Hartmann record C, 58·0, 58·2; H, 7·4, 7·2%).

Ozonolysis of Methyl and Ethyl $\Delta^{\alpha\epsilon}$-Hexadiene-ααγγδδζζ-octacarboxylate [*Methyl and Ethyl* (1 : 1 : 2)-bicyclo*Hexane*-1 : 1 : 3 : 3 : 4 : 4 : 6 : 6-*octacarboxylate*].—A solution of the methyl ester (5 g.) in chloroform (50 c.c.) at 0° was treated with ozonised oxygen for 24 hours. Some oxalic acid which had separated was collected, and the filtered chloroform solution was evaporated. The oily residue on boiling with water went almost completely into solution, but a turbidity appeared later and, on cooling, crystalline methyl ethanetetracarboxylate (0·9 g.) separated. Crystallised from acetone, it had m. p. 135°, and was identified first by analysis [Found : C, 45·8; H, 5·5; *M* (Rast), 262, 269. Calc. : C, 45·8; H, 5·4%; *M*, 262], and afterwards by its mixed m. p. with an authentic specimen, and by the products of its hydrolysis and decarboxylation. The mother-liquor from the decomposition with water yielded a further considerable quantity of oxalic acid, which was separated as calcium salt. It also yielded an oil, which on distillation gave a further quantity of crystalline methyl ethanetetracarboxylate. Similar results were obtained when the ozonide was reduced with zinc and acetic acid. The octa-ethyl ester was converted into ethyl ethanetetracarboxylate (m. p. and mixed m. p. 76°) and oxalic acid by the same method.

Methyl 3-*Methoxy*-2 : 2 : 4 : 4 : 5 : 5-*hexacarboxy*cyclo*pentane*-1-*malonate*.—The octamethyl ester (10 g.) was dissolved in a solution of sodium methoxide prepared from sodium (0·8 g.) and methyl alcohol (130 c.c.), and the product was precipitated by addition of dilute aqueous acid. Crystallised from acetone, the *methoxy*-compound had m. p. 193° (yield, 4 g.). The same compound was prepared from the octamethyl ester (0·5 g.) by treatment for 3 days with a cold solution of potassium hydroxide (0·5 g.) in methyl alcohol (50 c.c.). It was also obtained when the octamethyl ester (2 g.) was boiled for 3 hours with a solution of potassium cyanide (0·5 g.) in methyl alcohol (50 c.c.), but not when methyl alcohol alone was used as the reagent. Again it was obtained in attempts to methylate the octamethyl ester with methyl-alcoholic sodium methoxide and methyl iodide, but only the unchanged octamethyl ester was recovered when dry sodium methoxide and methyl iodide were employed with benzene as diluent. (Certain incidental observations of this kind are mentioned because no systematic account of the numerous negative experiments summarised in the introduction is included in this experimental account.) The methoxy-ester [Found : MeO (Zeisel), 47·5; C, 47·7, 47·6; H, 5·2, 5·0. $C_{23}H_{30}O_{17}$ requires MeO, 48·3; C, 47·75; H, 5·2%] was unaffected on treatment with permanganate, bromine, boiling ordinary concentrated nitric acid, or cold concentrated sulphuric acid. It was attacked by prolonged treatment with ozone, but the products could not be recognised.

Thermal Decomposition of Methyl $\Delta^{\alpha\epsilon}$-Hexadiene-ααγγδδζζ-octacarboxylate [*Methyl* (1 : 1 : 2)-bicyclo*Hexane*-1 : 1 : 3 : 3 : 4 : 4 : 6 : 6-*octacarboxylate*].—Decomposition set in above 200°, and a considerable quantity of the product distilled at 220—229°/18—20 mm. This was a viscous yellow oil, which partly solidified on keeping. The drained solid was crystallised from light petroleum, and identified as methyl 6-methoxy-α-pyrone-3 : 5-dicarboxylate, m. p. 129°, by comparison and mixed m. p. with an authentic specimen. As confirmation the pyrone was converted by means of ammonia into methyl hydrogen 6-methoxy-2-pyridone-3 : 5-dicarboxylate, m. p. 183° (Found : C, 47·7; H, 4·1; N, 6·2. Calc. : C, 47·6; H, 4·0; N, 6·2%).

Methyl and Hexamethyl Dihydrogen 2 : 2 : 4 : 4 : 5 : 5-*Hexacarboxy*cyclo*pentane*-1-*malonate*.—A solution of the octamethyl ester, m. p. 139°, (5 g.) and concentrated sulphuric acid (2 c.c.) in anhydrous methyl alcohol (200 c.c.) formed the catholyte, and dilute sulphuric acid formed the anolyte of an electrolytic cell. The solutions, each of which was kept cool by means of spiral tubes containing flowing water, were separated by a porous pot. The anode, a rod of lead, was placed inside the pot, and the cathode, a pool of mercury, outside. Electrolysis was effected with a current of 0·8—0·9 amp. passed for 24 hours, and the catholyte was then evaporated. The product was partly solid, and the drained crystals, after recrystallisation from methyl alcohol and acetone, yielded the *methyl dihydro-ester* in flat prisms, m. p. 149° [Found : C, 48·4;

H, 5·1; *M* (cryoscopic in benzene), 560, 570. $C_{22}H_{28}O_{16}$ requires C, 48·2; H, 5·15%; *M*, 548]. The liquid product which accompanied this ester deposited further quantities of the crystalline substance on keeping, and was then distilled. It had b. p. 142—143°/0·45 mm., reduced cold permanganate, and did not give satisfactory analytical figures, but on keeping continued slowly to deposit crystals of the ester of m. p. 149°. The ***hexamethyl acid-ester*** was obtained by boiling the neutral dihydro-ester (1 g.) with 20% hydrochloric acid (30 c.c.); after about 1·5 hours the neutral ester went into solution and the acid-ester began to crystallise. Collected from the cooled solution and crystallised from acetone, it had m. p. 252° (decomp.) (Found: C, 46·4; H, 5·0. $C_{20}H_{24}O_{16}$ requires C, 46·2; H, 4·65%).

2 : 4 : *5-Tricarboxy*cyclo*pentane-*1-*acetic Acid*.—The above acid-ester (0·5 g.) was boiled with a 10% solution of potassium hydroxide in ethyl alcohol (10 c.c.) containing just enough water to cause complete solution. After 6 hours the solution was allowed to cool and kept over-night. Crystals of a potassium salt which then separated were collected, dissolved in water, and treated with hydrochloric acid, and the solution thns obtained was evaporated to dryness over sulphuric acid in a vacuum. The required *acid* was obtained from the residue by extraction with acetone and crystallisation from alcohol. It had m. p. 225°, and was stable towards alkaline permanganate (Found: C, 46·5; H, 5·0. $C_{10}H_{12}O_8$ requires C, 46·2; H, 4·65%). The *silver* salt (Found: C, 17·6; H, 1·6; Ag, 58·6. $C_{10}H_8O_8Ag_4$ requires C, 17·45; H, 1·2; Ag, 62·8%) was converted by means of methyl iodide into the methyl ester, and this by treatment with ammonia into the *amide*, which, crystallised from water, had m. p. 280° (decomp.) (Found: C, 46·2; H, 6·1; N, 21·3. $C_{10}H_{16}O_4N_4$ requires C, 46·8; H, 6·3; N, 21·8%).

Dehydration and Reduction of Methyl 3-*Hydroxy*-2 : 4 : *5-tricarboxy*cyclo*pentane*-1-*acetate*.—The ester (10 g.) was heated with dry, powdered potassium hydrogen sulphate (35 g.) for 20 hours at 180°. The product was lixiviated with ether, and the filtered extract was dried with potassium carbonate and evaporated. The residual oil was distilled under reduced pressure in order to remove coloured products, and the colourless distillate was fractionally distilled (1 mm.). The principal fractions had severally b. p. 175—185° (1·7 g.) (Found: C, 54·0; H, 5·6%), b. p. 185—195° (6·5 g.) (Found: C, 53·7; H, 6·0. $C_{14}H_{18}O_8$ requires C, 53·5; H, 5·8%), b. p. 195—200° (0·5 g.) (Found: C, 53·4; H, 5·7%). All fractions instantly decolorised permanganate in acetone, and are assumed to consist essentially of mixtures of isomeric methyl 2 : 4 : 5-tricarboxy*cyclo*pentene-1-acetates. They absorbed about the correct amount of hydrogen on catalytic reduction. The large central fraction was hydrogenated with the aid of Adams's catalyst (1·5 g.) in methyl alcohol. Reduction was complete within 0·5 hour, and the product, which was stable to permanganate in acetone, was fractionated (2·5 mm.). The fractions had severally b. p. below 185° (0·3 g.), b. p. 185—187° (4·2 g.) (Found: C, 53·1; H, 6·6. $C_{14}H_{20}O_8$ requires C, 53·15; H, 6·4%), b. p. 187—190° (0·5 g.) (Found: C, 53·2; H, 6·6%). The last two fractions were hydrolysed by means of aqueous methyl-alcoholic potassium hydroxide, but the main product was an intractable gum, which did not decolorise alkaline permanganate.

Throughout this experimental record duplicate analyses refer to independent preparations.

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31. *The Elimination of Chlorine in the Hydrolysis of Aqueous Solutions of Chloroacetic Acid and the Chloroacetates.*

By H. M. Dawson and E. R. Pycock.

In previous papers (Dawson and Dyson, J., 1933, 49, 1133; 1934, 778) an account has been given of kinetic observations relative to the removal of bromine from the $CH_2Br\cdot CO_2$ group in neutral, acid, and alkaline solution. By making use of solutions with a constant total-salt concentration and by restricting the measurements of velocity to the very early stages of the reaction (0·5—2%), the complications arising from inert-salt effects and from the intervention of the reaction products have been largely avoided. In these circum-

stances it was found that the kinetic data can be satisfactorily interpreted in terms of four independent reactions corresponding with the equation

$$v = v_1 + v_2 + v_3 + v_4 = k_1[A'] + k_2[A']^2 + k_3[HA] + k_4[HA][A'] \quad . \quad . \quad (1)$$

in which [A'] and [HA] represent the concentrations of the bromoacetic ion and the undissociated bromoacetic acid respectively. The coefficients k_1 and k_3 probably correspond with reactions in which the solvent molecules are involved, and include the molar concentration of the water.

The experiments to be described show that analogous processes are effective in the elimination of chlorine from the $CH_2Cl{\cdot}CO_2$ group in aqueous solution. The evidence for this is provided by measurements of the initial velocity in solutions which contain (A) undissociated molecules only, (B) ions only, and (C) both molecules and ions. These were made at 45° and for the most part also at 25° with solutions in which the total-salt concentration was kept constant at 1 g.-equiv. per l. by the requisite addition of sodium nitrate.

(*A*) When the hydrogen-ion concentration of a moderately dilute solution of chloroacetic acid is sufficiently raised by the addition of a suitable strong acid (nitric acid), the concentration of the chloroacetic ions is reduced below the limit at which they play any effective part, and in these circumstances the initial velocity is found to be proportional to the concentration (x) of the chloroacetic acid as required by the third term $v = v_3 = k_3[HA]$ of equation (1). This is evident from the results in Table I.

TABLE I.

Velocities for xM-$CH_2Cl{\cdot}CO_2H$ + 0·5M-HNO_3 + 1·0M-$NaNO_3$ (45°).

x	0·0204	0·0306	0·050	0·0612	0·0707	0·0909
$10^7 \times v_{obs.}$	0·238	0·360	0·572	0·715	0·829	1·06
$10^7 \times v_{calc.}$	0·239	0·358	0·585	0·716	0·827	1·06

The above calculated velocities are based on $k_3 = 11{\cdot}7 \times 10^{-7}$, but it is probable that this value is affected to some extent by the presence of the nitric acid, in that the experimental data for solutions in which the ionisation of the chloroacetic acid is reduced by the addition of chloroacetate lead to the higher value $k_3 = 13{\cdot}5 \times 10^{-7}$. The depressing effect of the nitric acid on k_3 is, however, difficult to estimate, for free chlorine appears when the concentration of the nitric acid is further increased. If perchloric acid is substituted for the latter, and sodium perchlorate for the nitrate, no free chlorine is formed, but the value of k_3 diminishes markedly as the concentration of the perchloric acid increases. With regard to the above discrepancy, it is noteworthy that the values obtained for k_3 at 25° by the two methods are much closer than at 45°, but the relations have not been further examined.

(*B*) Solutions which contain the reactive group entirely in the ionic form are represented by neutral solutions of chloroacetate and in this case the general equation for the velocity reduces to the form $v = v_1 + v_2 = k_1x + k_2x^2$. Measurements in which the ionic concentration (x) was varied from 0·02 to 1·0 g.-equiv./l. have given results in close agreement with this equation, according to which v/x is a linear function of the chloroacetate concentration x. The actual graphs lead to the values of k_1 and k_2 shown in Table II, which affords a comparison of the calculated and the observed initial velocities.

TABLE II.

Velocities for xM-$CH_2Cl{\cdot}CO_2Na$ + $(1 - x)M$-$NaNO_3$.

Temp. 45°; $k_1 = 16{\cdot}5 \times 10^{-7}$, $k_2 = 57{\cdot}0 \times 10^{-7}$.

x	0·02	0·04	0·05	0·07	0·10	0·15	0·20	0·30
$10^7 \times v_{obs.}$	0·36	0·76	0·97	1·47	2·22	3·81	5·57	9·95
$10^7 \times v_{calc.}$	0·35	0·75	0·97	1·43	2·22	3·76	5·58	10·1
x	0·40	0·50	0·60	0·70	0·80	0·90	1·00	
$10^7 \times v_{obs.}$	15·5	22·4	30·1	39·0	49·5	61·4	73·6	
$10^7 \times v_{calc.}$	15·7	22·4	30·4	39·5	49·7	61·0	73·5	

Temp. 25°; $k_1 = 0{\cdot}95 \times 10^{-7}$, $k_2 = 3{\cdot}9 \times 10^{-7}$.

x	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
$10^7 \times v_{obs.}$	0·13	0·34	0·63	0·99	1·44	1·99	2·52	3·22	4·00	4·91
$10^7 \times v_{calc.}$	0·134	0·345	0·635	1·00	1·45	1·97	2·58	3·26	4·01	4·85

From the results in the above table it is apparent that the initial rate of chloride formation in neutral chloroacetate solutions can be adequately represented in terms of the two reactions corresponding with v_1 and v_2. The close agreement suggests that there can be no appreciable difference between the inert-salt effects produced by the nitrate and the chloroacetate.

(*C*) For solutions which contain both the acid and the salt in comparable quantities, the observed initial velocity is usually much greater than the sum of the velocities for the two corresponding solutions which contain only the acid or the salt. The difference increases with the product of the two concentrations, and this suggests that chloride is produced by the interaction of ions and molecules as represented by $v_4 = k_4[A'][HA]$ in equation (1).

When the acid and the salt are present in equivalent concentration (x), this equation reduces to the form $v = (k_1 + k_3)x + (k_2 + k_4)x^2$, and in accordance with this, the experimental data yield a straight line when v/x is plotted against x. The slope of this gives the value of $(k_2 + k_4)$, and the intercept gives $(k_1 + k_3)$. In combination with k_1 and k_2 of Table II, these lead to the values of k_3 and k_4 which have been used in the calculation of the partial and total velocities recorded in subsequent tables.

TABLE III.

Velocities for xM-$CH_2Cl \cdot CO_2H$ + xM-$CH_2Cl \cdot CO_2Na$ + $(1 - x)M$-$NaNO_3$.

Temp. 45°; $k_1 = 16{\cdot}5 \times 10^{-7}$, $k_2 = 57{\cdot}0 \times 10^{-7}$, $k_3 = 13{\cdot}5 \times 10^{-7}$, $k_4 = 220 \times 10^{-7}$.

x	0·02	0·04	0·10	0·20	0·30	0·40	0·50	0·60	0·80	1·00
$10^7 \times v_1$	0·33	0·66	1·65	3·30	4·95	6·60	8·25	9·90	13·2	16·5
$10^7 \times v_2$	0·02	0·09	0·57	2·28	5·13	9·12	14·3	20·5	36·5	57·0
$10^7 \times v_3$	0·27	0·54	1·35	2·70	4·05	5·40	6·75	8·10	10·8	13·5
$10^7 \times v_4$	0·09	0·35	2·20	8·80	19·8	35·2	55·0	79·2	141	220
$10^7 \times v_{calc.}$	0·71	1·64	5·77	17·1	33·9	56·3	84·3	118	201	307
$10^7 \times v_{obs.}$	0·72	1·68	5·91	17·2	34·5	57·2	84·8	117	193	298

Temp. 25°; $k_1 = 0{\cdot}95 \times 10^{-7}$, $k_2 = 3{\cdot}9 \times 10^{-7}$, $k_3 = 0{\cdot}69 \times 10^{-7}$, $k_4 = 15{\cdot}0 \times 10^{-7}$.

x	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80	0·90	1·00
$10^7 \times v_1$	0·095	0·19	0·28	0·38	0·47	0·57	0·66	0·76	0·85	0·95
$10^7 \times v_2$	0·039	0·16	0·35	0·62	0·97	1·40	1·91	2·50	3·16	3·90
$10^7 \times v_3$	0·069	0·14	0·21	0·28	0·34	0·41	0·48	0·55	0·62	0·69
$10^7 \times v_4$	0·150	0·60	1·35	2·40	3·75	5·40	7·35	9·60	12·1	15·0
$10^7 \times v_{calc.}$	0·35	1·09	2·19	3·68	5·55	7·79	10·4	13·4	16·8	20·5
$10^7 \times v_{obs.}$	0·36	1·11	2·26	3·73	5·65	7·99	10·5	13·6	16·9	20·7

From Table III it is apparent that v_1 and v_3 are jointly responsible for about 85% of the observed velocity when $x = 0{\cdot}02$, but that this diminishes to less than 10% when $x = 1$. In spite of the wide variations in the relative importance of the component reactions, the concordance between $v_{calc.}$ and $v_{obs.}$ is good over the entire range.

Observations have also been made with series of solutions in which the ion concentration is kept constant whilst that of the acid molecule is varied. If the ratio of acid to salt is not too large, the ionisation of the acid may be neglected, and the reaction velocity is found to be a linear function of the concentration of the acid as required by equation (1) in these circumstances. The results for two such series of solutions are given in Table IV.

TABLE IV.

$0{\cdot}2M$-$CH_2Cl \cdot CO_2Na$ + xM-$CH_2Cl \cdot CO_2H$ + $0{\cdot}8M$-$NaNO_3$ (45°).

x	0	0·05	0·10	0·15	0·20	0·25	0·30
$10^7 \times v_{obs.}$	5·60	8·53	11·4	14·3	17·2	20·0	22·9
$10^7 \times v_{calc.}$	5·58	8·46	11·3	14·2	17·1	20·0	22·8

$0{\cdot}4M$-$CH_2Cl \cdot CO_2Na$ + xM-$CH_2Cl \cdot CO_2H$ + $0{\cdot}6M$-$NaNO_3$ (25°).

x	0	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40
$10^7 \times v_{obs.}$	0·99	1·34	1·68	2·02	2·36	2·71	3·10	3·40	3·73
$10^7 \times v_{calc.}$	1·00	1·34	1·67	2·01	2·34	2·68	3·01	3·34	3·68

The concordance between the observed and the calculated velocities for the molecule-free solutions of Table II, and for the solutions containing molecules and ions of Tables III

and IV, shows no appreciable difference, and there can be little doubt that the constancy of the total-salt concentration of the solutions is partly responsible for the simplicity of the relations which have been found. In Table III the concentration of chloroacetic acid shows, however, a large variation (0·02—1·0 mol. per litre), and this represents a change in the reaction medium which might reasonably be expected to have an appreciable influence on the magnitude of the several velocity coefficients. In the more concentrated solutions of this series, the observed rate of change is mainly due to the partial velocities v_2 and v_4, and hence it would seem legitimate to infer that the coefficients k_2 and k_4 for the ion–ion and the molecule–ion reaction are not much affected by the change in the medium resulting from the presence of chloroacetic acid.

The behaviour of solutions of chloroacetic acid which contain no chloroacetate is not nearly so simple, in that the measured velocities for the more concentrated solutions are appreciably less than the calculated values. For these solutions, the initial velocity cannot be determined directly, because the hydrochloric acid which is formed reduces the concentration of the chloroacetate ion and thus has a very marked retarding effect on the reaction rate in the very early stages of hydrolysis. The required velocity has been obtained by a method which involves the measurement of the mean velocities for successive short periods corresponding with the liberation of 0·5, 1·0, 1·5, and 2·0% of the total chlorine. These mean velocities when plotted against the corresponding hydrochloric acid concentrations give a straight line which on extrapolation to [HCl] = 0 leads to a value for the true initial velocity. The disturbing effect in question increases with the concentration of the chloroacetic acid and is almost negligible when the solution is less than 0·1*M*.

The results for 0·1—1·0*M* solutions of chloroacetic acid at 45° and 25° are given in Table V. The calculated velocities derived from equation (1) are based on degrees of ionisation given by $K_c = 2{\cdot}40 \times 10^{-3}$, which is the value of the ionisation constant indicated by measurements of the rate of hydrolysis of ethyl acetate in 1*M*-sodium chloride solution at 25° with chloroacetic acid as catalyst (Dawson and Lowson, J., 1929, 393). Since the ionisation of acetic acid is very nearly the same in equivalent solutions of sodium chloride and sodium nitrate, it is assumed that this value of K_c will apply to the standard salt solutions used in the present experiments, and also that the influence of temperature can be neglected.

TABLE V.

Velocities for xM-$CH_2Cl{\cdot}CO_2H$ + 1·0*M*-$NaNO_3$.

	x	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
45°	$10^7 \times v_{obs.}$	1·54	3·17	5·24	7·05	9·02	11·1	—	14·8	—	18·9
	$10^7 \times v_{calc.}$	1·49	3·28	5·22	7·30	9·51	11·8	—	16·8	—	22·1
25°	$10^7 \times v_{obs.}$	0·098	0·212	0·326	0·459	0·582	0·708	0·840	0·984	1·12	1·24
	$10^7 \times v_{calc.}$	0·091	0·201	0·322	0·453	0·593	0·740	0·895	1·05	1·22	1·39

In explanation of the systematic divergence between $v_{obs.}$ and $v_{calc.}$ for the more concentrated solutions which contrasts very markedly with the concordance shown by the corresponding solutions in Table III, it may be noted that the observed velocities in Table V are mainly due to $v_3 = k_3[HA]$ and $v_4 = k_4[HA][A']$. The results in Table III suggest that k_4 is not affected by the chloroacetic acid content of the reaction medium, but on the other hand, there are grounds for the belief that the ionisation constant K_c in the case of the weaker acids falls appreciably as the concentration increases, and if this occurs with chloroacetic acid, it may be expected that v_4 will be reduced as a result of the lower value of [A'].

Such diminution in the value of K_c will have relatively little influence on v_3, but, on the other hand, there is evidence to support the view that k_3 becomes smaller as the concentration of the chloroacetic acid increases. If the hydrogen-ion concentration of the series of solutions in Table V is increased by the addition of a small amount of a strong acid (*e.g.*, 0·2*M*-perchloric acid), the resulting fall in the concentration of the chloroacetic ion leads to a very considerable diminution in the importance of v_4 as compared with v_3, but the divergence between the values of $v_{obs.}$ and $v_{calc.}$ is still in evidence at the higher concen-

trations. It thus appears that k_3 is reduced by the presence of chloroacetic acid in much the same way as it is by the strong acids, nitric and perchloric, to which reference has already been made (p. 154). This reduction is probably due, in part, to the fall in the concentration of the water which is inevitably associated with an increase in the chloroacetic acid content of the solution, for it is to be remembered that k_3 is in all probability represented by the product $k_3'[H_2O]$, where k_3' is the bimolecular coefficient corresponding with the interaction of the molecules of water and chloroacetic acid. The above considerations seem to offer a reasonable explanation of the medium effects which are responsible for the discrepancy between the observed and calculated velocities in the case of the more concentrated solutions of the free acid.

In further support of the view that the observed rate of formation of chloride by the hydrolysis of aqueous chloroacetate solutions can, in general, be accounted for in terms of the four reactions represented by equation (1), a brief reference may be made to the results obtained with a series of solutions in which chloroacetic acid is gradually replaced by sodium chloroacetate. Such a series corresponds with the general formula $(a - x)M\text{-}CH_2Cl{\cdot}CO_2H + xM\text{-}CH_2Cl{\cdot}CO_2Na$, in which a represents the total chloroacetic concentration. Provided that x/a be not too small, equation (1) for this series takes the form

$$\begin{aligned} v &= k_1x + k_2x^2 + k_3(a - x) + k_4x(a - x) \\ &= k_3a + (k_1 + k_4a - k_3)x - (k_4 - k_2)x^2 \end{aligned}$$

according to which the velocity passes through a maximum when $x = (k_1 + k_4a - k_3)/2(k_4 - k_2)$. On substitution of the numerical values of the velocity coefficients, it is found that the maximum velocity corresponds with the neutralisation of a fraction given by $x/a = 0{\cdot}675 + 0{\cdot}0092/a$. Table VI gives the results for such a series with $a = 1$.

TABLE VI.

x	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
$10^7 \times v_{obs.}$	18·9	32·5	48·9	63·7	74·6	84·3	88·7	90·5	88·6	83·4	73·6
$10^7 \times v_{calc.}$	22·1	34·2	51·6	65·7	76·6	84·2	88·6	89·7	87·6	82·2	73·5

The curve obtained by plotting $v_{obs.}$ against the fraction of neutralised acid x passes through a maximum in the neighbourhood of $x = 0{\cdot}70$, whilst the theoretical relation leads to $x = 0{\cdot}685$. The divergence between $v_{obs.}$ and $v_{calc.}$ at the lower values of x is, of course, to be attributed to the influence of those factors which have been discussed in connexion with the results in Table V.

Apart from secondary disturbances due to uncompensated changes in the reaction medium, the experimental data in the previous tables seem to justify the conclusion that equation (1) includes all the collisional processes which lead to the separation of covalent chlorine from the $CH_2Cl{\cdot}CO_2$ group in the form of the chloride ion. The processes in which the water molecule appears to be involved are much less effective than the other two processes, as may be seen if the values of the bimolecular velocity coefficients are compared. The relative values at 45° are :

Reactants	Mol.–H_2O.	Ion–H_2O.	Ion–Ion.	Mol.–Ion.	Mol.–Mol.
Relative bimol. vel. coeffs.	1	1·22	228	880	(0)

The kinetic measurements afford no evidence of the liberation of chlorine by collisions in which the hydrogen ion takes part or by collisions between pairs of chloroacetic acid molecules. If the effectiveness of such intermolecular collisions, as measured by the bimolecular velocity coefficient, is of the same order of magnitude as that for the molecule–water collisions, it is evident that the high concentration of the solvent molecules would preclude the detection of any effect which might result from collisions between pairs of chloroacetic acid molecules. The relations disclosed are similar to those for the liberation of bromine ion, but further data are required for the discussion of the quantitative differences.

EXPERIMENTAL.

The general method of experiment has been previously described (*loc. cit.*). Since, however, chloride cannot be determined accurately by the Volhard method, Drechsel's procedure (*Z. anal.*

Chem., 1877, **16**, 351) was adopted. The samples of reaction mixture were run into a measured volume of $M/20$-silver nitrate mixed with sufficient nitric acid to coagulate the silver chloride on stirring. This was filtered off, thoroughly washed, and the filtrate titrated with thiocyanate. This procedure increases considerably the volume of the solution, but apart from a loss of sharpness, the dilution does not affect the end-point. The same method was followed in the use of carefully purified potassium chloride for the standardisation of the silver solution.

SUMMARY.

Measurements of the rate at which chloride is liberated from the $CH_2Cl{\cdot}CO_2$ group show that in aqueous solution it is, in general, due to the four independent processes represented by the equation $v = k_1[A'] + k_2[A']^2 + k_3[HA] + k_4[HA][A']$. The first and the third term represent, in all probability, bimolecular processes in which the water molecule is involved. The experimental data relate to conditions in which there are no disturbances resulting from the products of reaction or from variations in the salt content of the reaction medium. Collisions in which the hydrogen ion is involved, and those between pairs of chloroacetic acid molecules, are not measurably effective.

THE UNIVERSITY, LEEDS. [*Received, December 9th*, **1935**.]

32. *Studies in Dielectric Polarisation. Part XVI. The Dipole Moments of Some Acid Halides and of Phosphorus Oxychloride.*

By GEORGE T. O. MARTIN and JAMES R. PARTINGTON.

ZAHN (*Physikal. Z.*, 1932, **33**, 686) measured the dipole moments of acetyl and chloroacetyl chlorides in the vapour state; the value found for the former, *viz.*, 2·68 (all values here and throughout are in Debye units), is in good agreement with that, 2·70, calculated by Højendahl (Thesis, Copenhagen, 1928, p. 128) from Pohrt's data (*Ann. Physik*, 1913, **42**, 569) —the values calculated from these data are generally too high. The moments of acetyl chloride and bromide and of propionyl, *n*-butyryl, *n*- and *iso*-valeryl chlorides have now been measured in benzene solution. The only possible impurity in the acid chlorides is a slight trace of phosphorus oxychloride remaining from the preparation, and the dipole moment of this compound was measured in order to ascertain if its presence would have any appreciable effect on the results. Since the moment found for chloroacetyl chloride in benzene solution was greater than that found by Zahn for the vapour state, it was measured again in carbon disulphide solution, and a value lower than that in the vapour state was found. The moment of trichloroacetyl chloride was measured in order to determine the direction of the ⁻COCl group moment.

The following values of μ have been found (all in benzene at 20°, unless otherwise stated):

Acetyl chloride	2·45	Acetyl bromide	2·43
Propionyl chloride	2·61	Chloroacetyl chloride	2·22
n-Butyryl chloride	2·61	Chloroacetyl chloride (in CS_2)	2·06
n-Valeryl chloride	2·61	Trichloroacetyl chloride	1·19
*iso*Valeryl chloride	2·63	Phosphorus oxychloride	2·40

The value 2·45 for acetyl chloride in benzene solution is considerably lower than that found in the vapour state, *viz.*, 2·68 and 2·70 (see above). This is a normal general result, but, in this case, the difference is larger than is usually found between the moments in the vapour state and in solution in benzene for a moment of this size; the values for acetone, *e.g.*, are: vapour 2·85 (Zahn, *loc. cit.*), solution 2·76 (Wolf and Gross, *Z. physikal. Chem.*, 1931, *B*, **14**, 305).

The value 2·68, which had been accepted as the moment of acetyl chloride, is considerably larger than that calculated from the C=O and the C—Cl moment (see Zahn, *loc. cit.*; Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697). These authors suggest that the high value can be explained by deformation of the tetrahedral symmetry of the mole-

cule, this causing a reduction of the angle between the two moments. Dornte (*ibid.*, 1933, **55**, 4126), by electron-diffraction measurements, has found the C—C—Cl angle in acetyl chloride to be 110° ± 10°, which, if the valencies are assumed to be symmetrical, gives a value for the Cl—C═O angle of 125° ± 10°. Smyth and McAlpine have shown that the value 2·68 for acetyl chloride can be explained in this way only on the assumption of the much smaller angle of 114·5°. We regard such a low value as improbable. Sutton (*Trans. Faraday Soc.*, 1934, **30**, 795), by taking the C═O moment as that of acetone, 2·75 (Wolf and Gross, *loc. cit.*), and the C—Cl moment as that of *tert.*-butyl chloride, 2·15 (Parts, *Z. physikal. Chem.*, 1930, *B*, **7**, 327; cf. van Arkel and Snoek, *ibid.*, 1932, *B*, **18**, 159)—both from measurements in solution—and the angle between them as 125°, calculates the moment of acetyl chloride to be 2·3. An examination of the vector diagram for the acetyl chloride molecule shows that a variation in the value taken for the C—Cl moment affects only slightly the magnitude of the resultant, but causes considerable variation in its direction. In order to calculate the moment of acetyl chloride, Smyth and McAlpine used for the C═O moment that of acetone (Zahn, *loc. cit.*; Stuart, *Z. Physik*, 1928, **51**, 490), and for the C—Cl moment that of methyl chloride, 1·86 (Sänger, *Helv. Phys. Acta*, 1930, **3**, 161; Fuchs, *Z. Physik*, 1930, **63**, 824), both determined in the vapour state. These two components acting at an angle of 125° to each other give a resultant of 2·35 acting at an angle of 15° to the C—C axis. A similar value can be calculated from solution measurements. Morgan and Lowry (*J. Physical Chem.*, 1930, **34**, 2385) find the moment of methyl chloride in carbon tetrachloride solution to be 1·65; the moment in benzene solution can therefore be assumed to be 1·7. A calculation similar to the above gives a resultant of 2·25 acting at an angle of 16° to the C—C axis. This angle is of importance in the calculation of the moments of chloroacetyl and trichloroacetyl chloride, which are discussed below.

The moment of propionyl chloride, 2·61, is greater than that of acetyl chloride, but the moment then remains constant as the homologous series is ascended. The induction which occurs in this series does not, therefore, extend beyond the second carbon atom in the chain, a result in accordance with that found by Cowley and Partington (Part XIII, J., 1935, 604) for the aliphatic nitriles and with that found for the alkyl halides (*ibid.*, Table III; also Mahanti, *Phil. Mag.*, 1935, **20**, 274). Although insufficient data for aldehydes are available to allow any conclusions to be drawn, Wolf and Gross (*loc. cit.*) found that the moments of many ketones are approximately equal. The induction effect, therefore, appears to depend on the presence of the C—Cl moment. The discrepancy between the calculated moment, 2·25, and the observed one, 2·45, for acetyl chloride in solution cannot be completely explained by assuming an action of the C═O moment on the C—Cl moment, or *vice versa*, and is probably due to the neglect of the effect of induction. That the COCl group exerts a powerful inductive effect is shown by the increase in moment from acetyl to propionyl chloride. This is probably a consequence of the action of the moment almost along the direction of the chain. It is, therefore, possible that the high value for the moment of acetyl chloride is due to induction in the C—C bond.

Dornte (*loc. cit.*) has found the Br—C—C angle in acetyl bromide to be 110° ± 10°, so if we apply the same argument to this compound, the moment should be almost identical with that of acetyl chloride. It is found to be 2·43, as compared with 2·45 for acetyl chloride. This small difference probably results from the fact that the C—Br moment is less than the C—Cl moment. The moment decreases in the series methyl chloride, bromide, iodide (see Table III, Part XIII, *loc. cit.*). For acetyl iodide, $P_{2\infty}$ was found to be 131 c.c., and by assuming the value 26·1 c.c. for P_E (Gustus and Stevens, *J. Amer. Chem. Soc.*, 1933, **55**, 374), the moment is calculated to be 2·22. The ease with which this compound decomposes renders the experimental result less accurate than the others, so that it is not entered in the table, but the compound would be expected to have a smaller moment than acetyl bromide, since the C—I moment is less than the C—Br moment.

The moments of chloroacetyl chloride in benzene (2·22) and in carbon disulphide (2·06) may be compared with the value (2·18) found for the vapour by Zahn, and suggest that his value may be a little too low. He found that this moment did not vary appreciably with temperature, a result which was explained by the fact that the COCl and the C—Cl

moment acted almost at right angles, which was shown by the vector diagram. Rotation about the C—C bond would not appreciably affect the moment. Application of Zahn's method (*Physikal. Z.*, 1932, **33**, 400) for the calculation of the dipole moments of molecules containing axes of rotation, on the assumption that the values of the COCl and the C—Cl moment are 2·45 and 1·70, respectively, gives the result 2·47. Since the observed value is 2·22, free rotation obviously does not occur. The minimum value of the moment was calculated as 2·05. It seems, therefore, that oscillations about the position of minimum moment occur.

In the calculation of the moment of trichloroacetyl chloride, it will first be assumed that the COCl moment acts at an angle of 15° to the direction of the C—C axis. The CCl_3 moment obviously acts along this axis but in the opposite direction. The COCl moment is taken as that of acetyl chloride, *viz.*, 2·45, and that of CCl_3 as that of methyl-chloroform, 1·57 (Sutton, *Proc. Roy. Soc.*, 1931, **133**, 668). These two moments acting at an angle of 165° to each other give a resultant of 1·1. If the COCl moment is assumed to act at an angle of 16° to the direction of the C—C axis, the result is 1·2, in good agreement with the observed value, 1·19. The value 16° is confirmed by the angle calculated from the moments of benzoyl chloride and *p*-nitrobenzoyl chloride, the results for which, together with those for other substituted benzoyl chlorides, will shortly be published.

The moment of phosphorus oxychloride, 2·40, can be regarded as the difference between the P ⟶ O and the PCl_3 moment, since these act in opposite directions. The moment of phosphorus trichloride was found by Smith (*ibid.*, 1932, **136**, 251) to be 1·16 in benzene solution (P_E being determined by the optical method). From this, the P ⟶ O moment is found to be 3·56, which is of the right order for a semipolar link between the phosphorus and the oxygen atom.

Experimental.

The dielectric constants were measured by means of the apparatus described in Parts XII and XIII (J., 1935, 602, 604). The dielectric cell is similar to that used in Part XII. It consists of two concentric glass cylinders sealed together at the top and bottom, with a separation of 1 mm., both ends of the inner one being sealed. Capillary tubes are sealed in at the top and bottom, as indicated in the figure. Liquid is introduced through the tube *B*, and the tube *A* has a mark and small expansion bulb, so that the complete cell resembles a single-bulb pykno-meter. The ends of the tubes *A* and *B* are fitted with ground-glass caps, and the cell is of such a size that it can be conveniently weighed on an ordinary balance for determination of densities. The plates consist of silver coatings deposited on the glass, contact being made with them by stout platinum wires sealed through the walls. The wire (*C*) from the inner plate passes up through the inner glass cylinder, which extends past the outer one, and is sealed through the top of the cell. The wire (*D*) from the outer plate is protected by a glass tube *E*, which runs parallel with the filling tube *B*, and is sealed at the top. These two platinum wires are bent over and dip into mercury cups on the screened lead from the standard condenser. Since the outer plate is earthed, no screening is necessary. The cell is supported in a water thermostat maintained at 20° ± 0·05°. The water level in the thermostat was kept constant, but within limits of ¼ inch the capacity of the cell was scarcely altered. The cell was connected with the standard condenser by lowering it through about 0·5 mm. so that the platinum wires dipped into the mercury cups. This was done by a spring-loaded screw mechanism clamped firmly to two rigid metal bars, the ends of which were fixed to the sides of the thermostat.

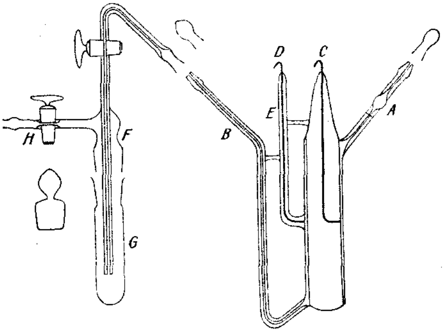
The whole of the inside of the cell was silvered to within a short distance of the top, this silver deposit being continuous. The silvering solution contained glucose as reducing agent (Sugden, J., 1933, 768). To obtain two separate plates, the silver was removed for a short distance at the bottom by means of a dilute chromic acid solution (0·5 g. $K_2Cr_2O_7$, 15 c.c. water, 10 drops conc. H_2SO_4), which was found to give good results and did not render the edges of the remaining silver liable to come away from the glass on washing with water. After removal of the acid, the cell was well washed with distilled water, dried by a current of air, and washed with the pure benzene used as solvent. Its volume was also determined by means of benzene, the density of which had been accurately determined. The capacity of the cell is 60 μμF, and its volume 9·4 c.c.

The densities of the solutions were determined to within 0·0001 by means of the cell, and

those of the pure substances by a 10 c.c. pyknometer, all at 20° ± 0·05°. The refractive indices were determined with a Pulfrich refractometer at the same temperature.

The symbols and method of calculation are the same as in previous parts of the series, the atomic polarisation being, as usual, left undetermined.

Preparation and Measurement of Solutions.—All possible precautions were taken to exclude moisture during the preparation and measurement of the solutions, since all the compounds are very readily hydrolysed. The solutions were prepared in glass vessels with ground-glass stoppers, one of which (*G*) is shown in the figure. The ground joints at the top of each vessel were interchangeable, so that all the vessels could fit a hollow stopper (*F*) through which a capillary passed. One end of the capillary dipped to the bottom of the vessel, and the other had a ground joint fitting the dielectric cell. A tap just above the stopper cut off the flow of liquid when the cell was full. The solutions were blown into the cell by a stream of dry air passed through a tube (*H*), fitted with a tap, sealed into the hollow stopper on to which the vessels fitted.



When a specimen of the compound having a constant b. p. had been obtained by fractionation, and its physical constants determined, it was distilled from a column with the condenser passing into a Brühl receiver, of the type used for vacuum distillation, which was closed by a calcium chloride tube. The carefully dried and weighed filling vessels were supported in holes in the rotating disc, so that the distillate could be collected in each vessel in turn, the amounts being estimated by counting the drops. The stoppers were then quickly inserted and the vessels removed from the receiver and weighed. 13 C.c. of dry benzene were poured quickly into each vessel from a measuring cylinder, the stoppers being removed for the shortest possible time. The vessels were then reweighed. The solutions were kept in a desiccator, and used as soon as possible after preparation. When they were being introduced into the cell, the stopper of the vessel was removed and quickly substituted by the hollow stopper carrying the filling tube, the solution being then blown into the cell. The capacity of the cell was measured as soon as the solution had reached the temperature of the thermostat. The interval of time required was reduced by keeping both the cell and the vessel containing the solution in the thermostat for some time before filling the cell. The capacity of the cell filled with a solution remained constant for several hours, except in the case of acetyl bromide and, to a less extent, acetyl chloride, where slight changes were detected after a time. When the capacity of the cell became constant, the liquid was adjusted to the mark, the cell removed from the thermostat, and its outside carefully dried. After attaining the temperature of the balance case, it was weighed.

Preparation of Materials.—Acetyl chloride and bromide, *n*-butyryl chloride, and chloroacetyl chloride were obtained from Kahlbaum and fractionated twice; *iso*valeryl chloride (Kahlbaum) was thrice fractionated. Propionyl and trichloroacetyl chlorides (Fraenkel and Landau) were fractionated twice.

n-Valeryl chloride was prepared from *n*-valeric acid previously fractionated twice; b. p. 185—186°/768 mm. The acid was treated with a slight excess of phosphorus pentachloride

and distilled, the *n*-valeryl chloride being isolated from the mixture by fractionating it four times through a very efficient column. Phosphorus oxychloride (Kahlbaum) was twice fractionated and then fractionally frozen.

The physical constants of the materials used are given below :

Compound.	B. p.	$D_{4°}^{20°}$.	$n_D^{20°}$.	$[R_L]_D$.
Acetyl chloride	50·6°/756 mm.	1·1044	1·3887	16·81
Propionyl chloride	78·3°/766	1·0565	1·4038	21·40
n-Butyryl chloride	101·5°/768	1·0205	1·4126	26·00
n-Valeryl chloride	126·9°/756	1·0004	1·4207	30·53
*iso*Valeryl chloride	115·5°/741	0·9862	1·4157	30·64
Acetyl bromide	75·6°/751	1·6503	1·4511	20·06
Chloroacetyl chloride	105·0°/750	1·4202	1·4541	21·40
Trichloroacetyl chloride	116·4°/755	1·6179	1·4701	31·37
Phosphorus oxychloride	106·3°/758 (m. p. 1·4°)	1·6748	1·4606	25·11

The following data are available for comparison : Acetyl chloride, b. p. 50·9° (corr.) (Thorpe, J., 1880, **37**, 188); $D_{4°}^{20°}$ 1·1051; $n_D^{20°}$ 1·3898 (Brühl, *Annalen*, 1880, **203**, 11); $D_{4°}^{20·6°}$ 1·1039; $n_D^{20·8°}$ 1·388 (von Auwers and Schmidt, *Ber.*, 1913, **46**, 473). Propionyl chloride, b. p. 77·8—78·3°/724 mm.; $D_{4°}^{20°}$ 1·0646; $n_D^{20°}$ 1·4051 (Brühl, *loc. cit.*). *n*-Butyryl chloride, b. p. 101·4—102° (Reiter, *Z. physikal. Chem.*, 1901, **36**, 137); $D_{4°}^{20°}$ 1·0277; $n_D^{20°}$ 1·4121 (Brühl, *loc. cit.*). *n*-Valeryl chloride, b. p. 127—128°; $D^{15°}$ 1·0155 (Freundler, *Bull. Soc. chim.*, 1894, **11**, 312). *iso*Valeryl chloride, b. p. 113·5—114·5°/726 mm.; $D_{4°}^{20°}$ 0·9887; $n_D^{20°}$ 1·4155 (Brühl, *loc. cit.*). Acetyl bromide, b. p. 75·1°/746 mm.; $D_{4°}^{15·8°}$ 1·6625; $n_D^{15·8°}$ 1·4537 (Karvonen, *Ann. Acad. Sci. Fenn.*, 1914, *A*, **5**, 62). Chloroacetyl chloride, b. p. *ca.* 105°; $D^{0°}$ 1·495 (Wurtz, *Ann. Chim. Phys.*, 1857, **49**, 60). Trichloroacetyl chloride, b. p. 118° (corr.) (Gal, *Bull. Soc. chim.*, 1873, **20**, 12); $D^{16·2°}$ 1·6291, $D_{4°}^{0°}$ 1·6564 (Thorpe, *loc. cit.*). Phosphorus oxychloride, b. p. 105·8°/753 mm. (Walden, *Z. anorg. Chem.*, 1900, **25**, 212); m. p. 1·38 (Partington, " Text-Book of Inorganic Chemistry," 1926, p. 635); $D_{4°}^{20°}$ 1·675 (I.C.T.), $n_D^{25·1°}$ 1·460 (Zecchini, *Gazzetta*, 1893, **23**, 97).

Benzene. Kahlbaum's " thiophen-free " benzene, dried over sodium and carefully fractionated, was used as solvent. For calibration of the dielectric cell, Kahlbaum's " molecular-weight " benzene, which had been subjected to the same treatment, was used.

Carbon disulphide. Hopkin and Williams's A.R. liquid was shaken with mercury till no further blackening occurred, and dried over and then fractionated from phosphoric oxide. It was used immediately after purification.

Results.—The solvent is benzene, except where otherwise stated, and all the measnrements are at 20°.

Acetyl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8790	2·281	26·57	—
0·00976	0·8807	2·364	27·70	141·3
0·01989	0·8824	2·450	28·83	139·2
0·03040	0·8843	2·540	29·95	136·8
0·03950	0·8859	2·618	30·87	134·7

$P_{2\infty}$ = 143·5 c.c.; P_E = 16·8 c.c.; μ = 2·45.

Propionyl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8784	2·276	26·52	—
0·01341	0·8807	2·403	28·31	160·0
0·02470	0·8825	2·507	29·71	155·8
0·03377	0·8841	2·590	30·78	152·8
0·04255	0·8855	2·671	31·79	150·4

$P_{2\infty}$ = 165·0 c.c.; P_E = 21·4 c.c.; μ = 2·61.

n-Butyryl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8784	2·276	26·52	—
0·02021	0·8814	2·471	29·35	166·8
0·03112	0·8833	2·578	30·81	164·5
0·04281	0·8850	2·694	32·33	162·4
0·04914	0·8861	2·758	33·13	161·2

$P_{2\infty}$ = 170·5 c.c.; P_E = 26·0 c.c.; μ = 2·61.

n-Valeryl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8792	2·280	26·55	—
0·00831	0·8804	2·359	27·77	173·1
0·01762	0·8816	2·448	29·09	170·7
0·02323	0·8824	2·501	29·86	169·2
0·03214	0·8837	2·586	31·08	167·4

$P_{2\infty}$ = 175·0 c.c.; P_E = 30·5 c.c.; μ = 2·61.

*iso*Valeryl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8792	2·280	26·55	—
0·01490	0·8812	2·425	28·75	174·3
0·02910	0·8831	2·563	30·75	171·1
0·04119	0·8847	2·681	32·39	168·2
0·05590	0·8867	2·826	34·31	165·5

$P_{2\infty}$ = 177·5 c.c.; P_E = 30·6 c.c.; μ = 2·63.

Acetyl bromide.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8784	2·276	26·52	—
0·01477	0·8880	2·405	28·27	145·1
0·02357	0·8941	2·486	29·31	145·1
0·03361	0·9001	2·580	30·49	144·8
0·03771	0·9030	2·620	30·97	144·6

$P_{2\infty}$ = 145·5 c.c.; P_E = 20·1 c.c.; μ = 2·43.

Chloroacetyl chloride.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8792	2·278	26·53	—
0·00941	0·8833	2·343	27·44	125·3
0·01739	0·8870	2·400	28·22	125·2
0·02735	0·8916	2·474	29·20	125·5
0·03568	0·8956	2·535	29·97	124·9

$P_{2\infty}$ = 125·5 c.c.; P_E = 21·4 c.c.; μ = 2·22.

Trichloroacetyl chloride.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8790	2·280	26·56	—
0·00705	0·8854	2·293	26·80	61·2
0·01408	0·8919	2·306	27·04	60·6
0·02108	0·8983	2·319	27·28	60·8
0·02839	0·9050	2·333	27·53	60·7

$P_{2\infty}$ = 61·5 c.c.; P_E = 31·4 c.c.; μ = 1·19.

Chloroacetyl chloride (in CS_2).

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	1·2635	2·637	21·27	—
0·00683	1·2641	2·704	21·89	111·7
0·01380	1·2648	2·773	22·51	111·5
0·01939	1·2654	2·832	23·02	111·6
0·02545	1·2660	2·895	23·56	111·4

$P_{2\infty}$ = 111·8 c.c.; P_E = 21·4 c.c.; μ = 2·06.

Phosphorus oxychloride.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8784	2·276	26·52	—
0·01797	0·8930	2·427	28·65	145·4
0·02800	0·9012	2·512	29·81	144·2
0·03909	0·9102	2·611	31·09	143·4
0·04505	0·9150	2·662	31·73	142·3

$P_{2\infty}$ = 147·5 c.c.; P_E = 25·1 c.c.; μ = 2·40.

SUMMARY.

The dipole moments of acetyl, propionyl, *n*-butyryl, *n*-valeryl, and *iso*valeryl chlorides have been measured, and it is shown that the moment increases in the series only as far as the second. An explanation for the large value of the moment of acetyl chloride has been suggested. The moments of acetyl bromide and iodide are compared with that of acetyl chloride. The moments of chloro- and trichloro-acetyl chloride can be explained on the assumption that the $C\!\lessdot^{O}_{Cl}$ moment acts at an angle of 16° to the direction of the C—C axis. From the moment of phosphorus oxychloride a value for the P ⟶ O moment is found.

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QUEEN MARY COLLEGE, UNIVERSITY OF LONDON.

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33. *The Electrolytic Preparation of Deuterium and the Separation Coefficient α.**

By MALCOLM P. APPLEBEY and GEOFFREY OGDEN.

IT has become increasingly evident during the past 18 months that the efficiency of electrolytic cells in the separation of the two isotopes of hydrogen falls far short of the value calculated from purely theoretical considerations. This calculation has been carried out by several investigators (Topley and Eyring, *J. Chem. Physics*, 1934, **2**, 217; Bowden and Kenyon, *Nature*, 1935, **135**, 105; Halpern and Gross, *J. Chem. Physics*, 1935, **3**, 453; Polanyi and Horiuti, *Nature*, 1933, **132**, 819, 931), who obtain values of α lying between 0·05 and 0·10. All these investigators are agreed that the rate-determining step in the process is the passage of the hydrogen or deuterium atom over an energy barrier, the non-classical passage through the barrier being supposed negligible. Experiment also shows that α is dependent to a certain extent on the electrode material and on the concentration of deuterium oxide in the electrolyte, whereas theoretically α should be practically independent of both these factors.

It is evident that these theories of over-voltage are not sufficient to account for the experimentally obtained values of α; if the theoretical value of 0·05—0·10 is correct, there

* The separation coefficient α referred to in this paper is the reverse of that usually employed by workers in this field. It is given by

$$\alpha = \frac{\text{concentration of deuterium in the gas phase}}{\text{concentration of deuterium in the liquid phase}}$$

at any instant, and is the separation coefficient employed by earlier workers.

must be some disturbing effect in the actual experimental determinations tending to give a much larger value of α than the true one. One such effect, and probably the most important, is the exchange reaction $HOD + H_2 \rightleftharpoons H_2O + HD$ (and in more concentrated solutions, $D_2O + H_2 \rightleftharpoons HOD + HD$, $D_2O + HD \rightleftharpoons HOD + D_2$). It is certain that such exchange reactions take place to some degree during electrolysis, since most metals used as electrode materials will catalyse this reaction. The catalytic effect may, indeed, be more vigorous under electrolytic conditions because the hydrogen is in an activated or nascent state. When the gas evolved contains more light hydrogen than is defined by the concentration determined from the equilibrium equation $K = [HD][H_2O]/[H_2][HOD] = 3{\cdot}8$ at room temperature, the experimentally determined value of α will be greater than the ideal value of the electrolytic separation coefficient α_0, and will, in fact, approach $1/K = 0{\cdot}270$. With certain metals which are good catalysts for the exchange reaction, the value of α obtained in electrolytic experiments is actually equal to 0·270, showing that equilibrium is established between the water and the gas as fast as the gas is liberated at the electrode surface. This behaviour is shown by platinum electrodes, the true electrolytic separation coefficient being completely suppressed owing to the rapidity of the catalytic exchange.

In the process of electrolysis, the concentration of hydrogen in the liquor in the neighbourhood of the cathode decreases, while that of deuterium increases, owing to the preferential electrolysis of the hydrogen. It is therefore evident that as electrolysis proceeds the local concentration of deuterium hydroxide in the neighbourhood of the cathode becomes much greater than that in the bulk of the solution; such local concentration not only in itself increases the proportion of deuterium liberated as gas, but also favours the exchange reaction by which the electrolytic separation is opposed.

These considerations have led the authors to the adoption of the following principles in the design of cells for the production of heavy water: (a) The metal used for the electrode material must be a poor catalyst for the exchange reactions; (b) the evolved hydrogen gas must be removed as quickly as possible from the electrode surface; (c) local concentration of deuterium hydroxide at the electrode surface must be avoided. The last two conditions can be attained by efficient stirring of the electrolyte either mechanically or by the gas evolution itself, the efficiency then depending largely on correct design of electrodes.

Two types of cell employing the latter device have been employed in production at the Billingham works of Imperial Chemical Industries, and are now described in the hope that they will be of service to other workers. The first is a small cell (Fig. 1 *a*) suitable for the later stages of concentration. It has electrodes consisting of concentric nickel cylinders, the outer cylinder fitting fairly tightly into the glass cell—the electrolysis taking place in the annular space (0·2 cm.) between the two cylinders. The whole cell is enclosed in a water-cooled jacket. During electrolysis, the liquor in the annular space, being much lighter than that in the inner hollow cylinder by reason of the gases it contains, rapidly rises and sets up a brisk circulatory motion which clears the gas away from the electrode surface and prevents any concentration gradients in the liquor itself. A series of experiments carried out in this type of cell, in which the only variant was the concentration of deuterium oxide in the electrolyte, gave the results recorded below. It is evident that α increases with increasing concentration—an effect to be expected since the exchange reaction will take place to a greater extent as the deuterium oxide concentration in the electrolyte increases. In these and all other experiments recorded in this paper, the electrolyte was sodium hydroxide of 5% initial concentration, and the current density 0·8 amp./cm.^{2}.

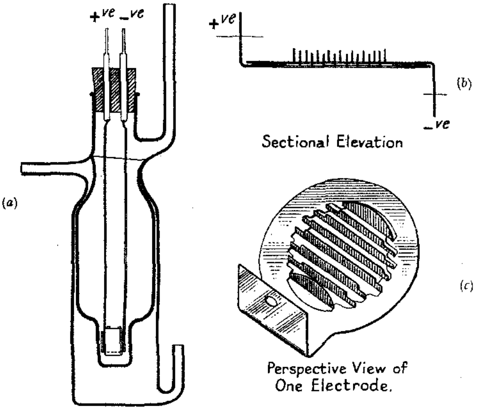
The temperature of the electrolyte was maintained at 13—15° by the circulation of tap water through the water-jacket of the cell. A spray trap was fitted to the cell, and was arranged so that any spray carried over by the gas was returned to the cell. In addition, the electrolytic gas passed through a reflux condenser through which ice-cold water circulated, any condensate from the gas being returned to the cell. At the conclusion of an experiment, the caustic liquor from the cell was neutralised with solid carbon dioxide, and the neutral product distilled from a copper vessel and then carefully purified. The oxygen isotope concentration of the product was "normalised" by bubbling a large volume of sulphur dioxide through it—precautions being taken to minimise any evaporation losses. The water was again distilled to free it from

dissolved sulphur dioxide, and its density determined by a float method similar to that employed by Emeléus *et al.* (J., 1934, 1207).

Mean concentration, %, of D_2O during electrolysis	3·7	29·5	58·75	86·5
Separation coefficient, α	0·19	0·18	0·23	0·29

The larger cell illustrated in Fig. 1 *b* and *c* is suited for the earlier stages of concentration. The electrodes of this cell consist of a number of parallel strips of nickel about 1 cm. high, which are alternately anode and cathode. The anode strips are all joined at their ends to a flat circular strip of thin nickel plate, about 2 cm. wide cut from a circle of 12 cm. diameter. The whole resembles a circular grating, the strips forming the grating varying in length, the outermost one on each side being the shortest and each grid electrode progressively increasing in length toward the centre. The cathode grid is built up in exactly the same way, and when the two composite electrodes are fitted together with a rubber washer between the two outer flat circular strips to

Fig. 1.



which the grids are joined, the vertical plates are alternately cathode and anode. The electrodes are contained in a glass sided cell with a metal base, the base being insulated from the electrodes by a rubber washer.

A representative series of results obtained with this cell is given in Table I.

Table I.

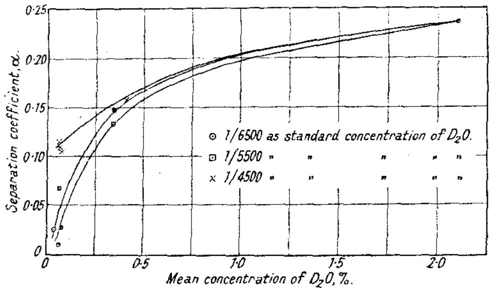
Spacing between the grids constituting electrodes	0·5 cm.
Material of which electrodes were constructed..................	nickel.
Concentration of deuterium in standard water	1 in 5500.

Initial vol. of electrolyte, ml.	Vol. after electrolysis, ml.	Concn. of D_2O initially in electrolyte.	Concn. of D_2O after electrolysis.	Separation coefficient, α.
1000	234	1/2950	1/730	0·029
1000	249	1/2800	1/708	0·010
1000	249	1/2600	1/695	0·014
1000	270	1/1295	1/512	0·120
1000	250	1/492	1/151	0·145
1000	216	1·34%	2·16%	0·236

With this cell at very low concentrations of deuterium oxide, the value of α obtained is very much lower than the predicted values obtained by various workers (0·05—0·10). These workers have, in their calculations, neglected the 'tunnel effect' and only taken

into account the different zero-point energies of the two hydrogen isotopes. Briefly, the tunnel or permeability effect follows as a direct consequence of the wave nature of matter. If a particle has an energy W, and the energy of activation required for a chemical change in that particle is E, then classical reaction kinetics stated that reaction would only take place if $W>E$ and would never take place if $W<E$. Quantum mechanics, however, states that there is a definite probability of reaction taking place even if $W<E$, the probability of reaction being a complex function of e^{E-W} and the width of the energy barrier. Ogden and Bawn (*Trans. Faraday Soc.*, 1934 **30**, 432) have calculated the electrolytic separation coefficient α, taking into account the probability of leakage through an energy barrier, and have shown that α may be as low as 0·013. A preliminary notice of these experiments has already been published by Polanyi and Horiuti (*Acta Physicochimica U.R.S.S.*, 1935, **2**, 505), who consider them to be one of the first authenticated proofs that quantum mechanical leakage is an important factor in the difference in rate of reaction of hydrogen and deuterium atoms. The authors are, however, of opinion that this conclusion can only be accepted provisionally at present, because the values of α calculated from experiments in very dilute solutions are largely affected by the particular value which is accepted for the concentration of deuterium in standard water.

Fig. 2.



To illustrate this point, we have calculated in Table II the electrolytic separation coefficient from a single determination, assuming successively a deuterium concentration of one in 4500, 5500, 6500, and 7500. Similar calculations performed with all the determinations of Table I lead to the curves plotted in Fig. 2, which show the variation of α with the mean concentration of deuterium during electrolysis* for the same assumed values of the deuterium concentration of standard water.

Various estimates of the concentration of deuterium oxide in normal water have been made, based upon either (*a*) the mass-spectrographic method or (*b*) the preparation of pure light water or protium oxide, $H_2{}^1O^{16}$. In the latter method, water is subjected to fractional electrolysis, fractional distillation, or a combination of both methods, until the final product contains a negligible amount of deuterium. In the electrolysis of water, the hydrogen evolved from the cathode contains less deuterium than the water. This hydrogen is burnt back to water by recombination with the evolved oxygen, and the water so formed utilised in the next stage of the electrolysis. The density of the water from each stage of

* It is easy to show that the mean concentration C during an electrolysis is

$$C_0(V_0 - V^{\alpha}V_0{}^{1-\alpha})/\alpha(V_0 - V)$$

where C_0 is the initial concentration of deuterium, and V_0 and V are the initial and the final volume This formula is approximate, being strictly true only for conditions in which the concentration of light water may be taken as constant and in which changes in α during the electrolysis may be regarded as negligible.

TABLE II.

Vol. of water before electrolysis = 1000 ml. (d, 20 × 10^{-6} greater than that of normal water).
Vol. of water after electrolysis = 234 ml. (d, 134 × 10^{-6} greater than that of normal water).

Assumed proptn. of D in standard water.	Initial concn. of D_2O in electrolyte.	Concn. of D_2O after electrolysis.	Separation coefficient, α.
1/4500	1/2520	1/697	0·107
1/5500	1/2725	1/701	0·067
1/6500	1/2950	1/716	0·026
1/7500	1/3145	1/727	– 0·009

electrolysis is measured until finally there is no change; the deuterium concentration will then be negligible. The density of the product after careful purification is measured, and if it is a p.p.m. lighter than ordinary or standard water, the deuterium content of the latter is given by $a/1079$. The figure 1079 is obtained from the density of pure deuterium oxide, given by Taylor and Selwood (*J. Amer. Chem. Soc.*, 1934, **56**, 998) as 1·1079. A more accurate figure has recently been published by Tronstad, Nordhagen, and Brun (*Nature*, 1935, **136**, 515), who give $d_{25°}^{25°} = 1{\cdot}1074$. This will alter the existing values of the concentration of deuterium oxide in standard water by about 0·5%—an amount which is negligible compared with the experimental error inherent in the methods employed for its determination.

This method is, however, complicated hy the fact that any process which fractionally separates the two isotopes of hydrogen also separates, though to a less degree, the isotopes of oxygen. The change in the abundance ratio of the oxygen isotopes causes a corresponding decrease in density of the water sample which evidently must be allowed for.

The commonest method employed is to restore the oxygen isotope ratio back to its normal value or to some known standard value, and this is most easily accomplished by making use of the isotopic reactions discovered by Lewis (*J. Amer. Chem. Soc.*, 1933, **55**, 3502). A gas such as sulphur dioxide is bubbled through the water sample, the isotopic reaction $SO_2{}^{16} + 2H_2O^{18} = SO_2{}^{18} + 2H_2O^{16}$ then taking place. If sufficient sulphur dioxide were bubbled through the water, it was formerly believed that the water recovered its normal abundance ratio with respect to the oxygen isotopes, and any difference in density after this treatment must be due to a shift in the hydrogen abundance ratio alone. Recently, however, Urey and Grieff (*ibid.*, 1935, **57**, 521) have shown that in this reaction there is a definite equilibrium—some enrichment of O^{18} occurring in the sulphur dioxide at the expense of the water. The enrichment is only very small, the factor being 1·014 at room temperature. Therefore, ordinary water treated with a large excess of sulphur dioxide will have a concentration of O^{18} of 1 part in 639 parts of oxygen instead of the normal value of 1 in 630. This effect was easily shown by taking a sample of tap water and, after careful purification, bubbling a large excess of sulphur dioxide through one portion of the sample. After repurification and redistillation, its density was found to be 3 p.p.m. lighter than the original sample, which agrees very well with the figure of 2·3 p.p.m. calculated from Urey and Grieff's results.

Gray and his co-workers (*Nature*, 1934, **134**, 661), by a combination of fractional electrolysis and distillation, obtained light water which was 12 p.p.m. lighter than ordinary water, corresponding to a concentration of deuterium oxide in normal water of 1/9000. Reference to Table II of the present communication shows that such a value is irreconcilable with our experiments, from which the assumption of any value less than 1/7000 for the deuterium concentration leads to negative values for the separation coefficient, which are, of course, impossible. Washburn, Smith, and Frandsen (*J. Chem. Physics*, 1933, **1**, 288), employing electrolytic methods, obtained water lighter than normal water by 18 p.p.m., and all this difference in density was due to loss of heavy hydrogen, which leads to a value of 1/6000 for the concentration in normal water. Recently, Johnson (*J. Amer. Chem. Soc.*, 1935, **57**, 484) prepared deuterium-free water by the electrolysis of a large volume of water —the initial 25% of the electrolytic gases evolved in each stage serving as the electrolyte in the next. The process was continued for five stages, and the allowance for the change in heavy-oxygen concentration was carried out graphically. It could be easily shown from a knowledge of the separation coefficient α of the electrolytic cell that, after the second

stage, the concentration of deuterium would be negligible, and so any further decrease in density must be due to the change in heavy-oxygen concentration—so that this change in concentration could then be allowed for in the first two stages of electrolysis. In this way, Johnson showed that the normal concentration of deuterium oxide in water is $1/5750 \pm 250$, which agrees very well with Bleakney and Gould's latest mass-spectrographic value, $1/5000 \pm 500$ (*Physical Rev.*, 1933, **44**, 265). The latest value for the concentration of deuterium oxide in normal water may be calculated from the results of Tronstad, Nordhagen, and Brun (*loc. cit.*), who prepared protium oxide containing less than 1 part in 200,000 of deuterium oxide. This water was 18·5 p.p.m. lighter than normal water, whence the concentration of deuterium oxide in ordinary water is found to be 1/5800, in good agreement with the generally accepted value.

A consideration of the evidence collected in the foregoing paragraphs leads us to the view that the most probable concentration of deuterium in standard water is 1 in 5500. If this figure, or any slightly lower value, is confirmed, our experiments leave no escape from the conclusion that quantum-mechanical leakage has been demonstrated. On the other hand, it must be pointed out not only that a value approximating to 1 in 4500 gives α at infinite dilution a value approximating to the ideal value without tunnelling, but also that such an assumption gives a curve for the variation of α with concentration which is simpler in form and inherently more probable. Which of these alternatives must be accepted can only be decided when more precise knowledge of the constitution of standard water has been obtained.

We acknowledge our indebtedness to Messrs. Imperial Chemical Industries Ltd., in whose laboratories at Billingham these investigations were carried out, for permission to publish the results.

BILLINGHAM-ON-TEES. [*Received, November 22nd, 1935.*]

NOTE.

Alkaline Halogenation. The Bromination of Sodium Benzoate. By P. L. HARRIS and J. C. SMITH.

OWING to the rapid decomposition of hypobromite solutions the bromination of sodium benzoate in aqueous solution gives varying results. In the correspondiug chlorination, which is much more rapid, substitution occurs iu the order $o > m > p$, an orientation attributed to the localised negative charge on the benzoate anion (Smith, J., 1934, 213). For bromination the ratios are probably nearer $o : m : p = 1$, but are not constant, since, when the reaction mixture becomes acid, the conditions are similar to those found by Stark (*Ber.*, 1910, **43**, 670) to favour bromination in the *m*-position. The use of two equivalents of alkali (giving the proportion Ph·CO_2Na : NaOBr) almost completely stops bromination, and a similar weakness of the hypochlorite ion as a chlorinating agent compared with halogen was observed in preliminary experiments (compare Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2340; Bartlett and Vincent, *ibid.*, 1935, **57**, 1596).

Benzoic acid (61 g.) in a solution of sodium hypobromite (2000 c.c., from 40 g. of sodium hydroxide and 80 g. of bromine) began after 2 days at 35° to deposit a solid (mainly *p*-bromobenzoic acid) and after 7 days (free bromine having been present continuously) the mixture was cooled and filtered. The mixture of acids obtained from the filtrate (largely unchanged benzoic acid) was esterified, and by methods similar to those used for the chlorobenzoic acids the total bromination was estimated to yield *o*-bromobenzoic acid 6 g., *m*- 5 g., and *p*- 7 g. In a second bromination under similar conditions the products were *o*-bromobenzoic acid 4 g., *m*- 6 g., and *p*- 4 g.

Repetition of the bromination of an aqueous suspension of benzoic acid with hypobromous acid (Stark, *loc. cit.*) confirmed the statement that the product was mainly *m*-bromobenzoic acid. Two successive treatments with hypobromous acid gave a product (Found: *M*, 188. Calc. for $C_7H_5O_2Br$, 201), m. p. 128·2°; the m. p. was depressed by admixture with *o*-bromobenzoic acid (5%) or *p*- (2%), but raised with *m*- (5%). The crude acid, twice crystallised from water and once from benzene, melted at 152—154° alone or mixed with *m*-bromobenzoic acid.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, November 19th, 1935.*]

OBITUARY NOTICES.

HARRY BOWES.

1869—1935.

BOWES was educated at the Manchester Grammar School, and articled to Messrs. Crace-Calvert and Thomson, Royal Institution, Manchester. He became chief chemist at those well-known chemical laboratories in 1887, and retained the position until, in 1893, he was appointed chemist at Messrs. J. F. Hill and Co.'s Bowker Bank Calico-Printing Works. He afterwards joined the Grossmann Cyanide Syndicate and conducted considerable research on the manufacture of cyanides.

In 1903, Bowes commenced business, in conjunction with Mr. W. Edgar Sims, M.Sc., as analytical and consulting chemist, eventually founding the business of the Reliance Manufacturing Company, at Radford Street, Blackley, Manchester, in which he was actively engaged until his death at the age of 66.

Bowes was admitted a Fellow of the Institute of Chemistry in 1894. He was a member of the International Society of Leather Trades Chemists, and for 30 years was analyst and consultant to the Manchester Board of Guardians. He was also consultant to the rubber-proofing, cotton, and leather trades, on the technical chemistry of which he was a recognised authority. He did much research work on cutting-tool lubricants; on the tanning and treatment of leather; and, in conjunction with Dr. Arnold Renshaw, on antiseptics and bacteriology; but he did not seek publicity and his work is not recorded in the technical journals. His energies were constantly directed towards improving the standard of his own manufactured products, with increasing success.

Bowes's recreations were golf and the cultivation of flowers. He was a Fellow of the Royal Horticultural Society and, of late years, spent most of his leisure time in his beloved garden. He was a man of outstanding personality, of high character and integrity in business; generous and open-handed to a degree. He will long be held in grateful remembrance by many friends who had the felicity to know him intimately. W. L. GADD.

SAMUEL HENRY CLIFFORD BRIGGS.

1880—1935.

SAMUEL HENRY CLIFFORD BRIGGS was the son of Joseph and Martha Ellen Briggs. He was born at Cleckheaton in Yorkshire on April 13th, 1880, and almost all his life was connected with this part of the highly industrial West Riding. His school days were spent at Ashville College, Harrogate, where he already displayed marked ability. He then proceeded to the Yorkshire College, Leeds, at that time a constituent College of the Victoria University. In 1900 he graduated B.Sc. in physics and chemistry and two years later he was awarded a First Class in the Honours School of Chemistry. The next year he obtained the degree of M.Sc. In that year he was elected to an 1851 Exhibition Scholarship, but owing to what he felt to be the greater claim of continuing the business connection established by his father he relinquished the scholarship, thus giving up a professional career in chemistry which was of great promise. Entering industrial life, he established a successful worsted spinning business at Providence Mills, Cleckheaton, and he was associated with his younger brother in the direction of it until his untimely death.

In 1914 Briggs married Margaret Hartley of Castleford and they had one daughter. Both his wife and his daughter survive him.

Although Briggs gave up a career in chemistry, he could not throw off the spell which his few years' research work at Leeds had cast over him. He fixed up a laboratory at home in a disused coach house and continued there investigations which he had begun at the Yorkshire College. The only time available was in the evenings and at week ends, but he made good use of it, as his considerable output of published papers, for one so situated, shows. All his work after he left Leeds was carried out in this home-made laboratory or in others which he subsequently made at Gomersal and in turn at Birstall, where he went to live after his marriage. He was still able to keep in touch with his former Leeds colleagues through the Priestley Club, a scientific club which meets at the University, and he attended its meetings with great regularity. In 1910 he was awarded the degree of D.Sc.

Although he kept up his interest in chemistry in this way and utilised a great deal of his spare time in its pursuit, he had other claims on his leisure. His business activities brought him into a sphere in which his qualities of mind and temper were highly prized and he was not long in becoming one of the trusted advisers in that particular section of the textile industry with which he was associated. It is therefore not surprising that he was chosen to represent the Worsted Spinning Section of the British Commercial Economic Mission which visited the Far East a few years ago. He also acted for a time as Chairman of the Chamber of Commerce of the Spen Valley and his scientific knowledge combined with his experience of the textile industry made him a much valued member of the Council of the Wool Industries Research Association which has its headquarters at Torridon in Leeds. At the time of his death he was Vice-Chairman of this Council. He had been a member of it and of its Research Control Committee for fifteen years.

Briggs's first three published papers were in the organic field and dealt with work which he carried out as a research student with Professor A. G. Perkin and the late Professor J. B. Cohen. During this period he became interested, and in later years intensely so, in the structure of inorganic compounds. One of the reasons which led to this was the attempt which he made, whilst still a post-graduate student, to prepare the normal chromates of copper, nickel and allied metals. Although this failed, he obtained some new double chromates containing these metals and they were described in a paper published in the *Transactions* in 1903. This was the first of a series, the last of which was published in 1929, which described the preparation, properties and significance, from the point of view of inorganic structure, of many new co-ordination compounds of chromium and molybdenum. His preoccupation with work of this character led him to consider the detailed structure of the compounds involved and in pursuance of the views on this subject which be expressed in 1908 he described in 1911 two forms of potassium ferrocyanide analogous to the α- and the β-form of the ferricyanide described by Locke and Edwards. After Bennett in 1917 had shown the α- and the β-ferrocyanides to be crystallographically indistinguishable, Briggs re-examined the matter and demonstrated that the β-ferricyanide was a compound of the true ferricyanide with the aquopentacyanoferriate, whereas the β-ferrocyanide was a mixture of ferrocyanide proper with a very small amount of aquopentacyanoferroate.

In later papers he pursued the theoretical aspects of co-ordination in their relation to the modern development of the theory of valency, publishing his last discussion of the matter in the *Philosophical Magazine* in 1926. In 1929 he contributed his last experimental work, which was concerned with chromatocobaltiammines.

This account will have shown that Briggs was a true representative of that type of highly competent amateur (in the best sense of the word) with which this country has been notably endowed in the past but which owing to the stress of modern life is unfortunately much less frequently encountered to-day.

The daily demands of business affairs and his chemical work did not leave him much leisure for other pursuits. He was not very successful at games, but music was one of his relaxations. He was a good pianist and Beethoven and Bach rather than the Moderns were his favourite composers. He got exercise by walking over his native moors, and the wilder and rugged landscape of the hill country made more appeal to him than the more comfortable and less exciting valleys. On such walks he was a good companion and those who trudged and talked with him on these occasions will not easily forget the breadth and range of his views, his essential gentleness of nature, and his rigid firmness where principles were concerned. His outlook on world affairs was flavoured somewhat by pessimism. He saw the great problems and had not much faith in man's efforts to solve them. Anything he took up himself he pursued with great zeal and fervour. He could not have achieved all he did without much more than ordinary industry and great constancy of purpose. It is greatly to be deplored that all these activities came to an end on August 24th, 1935, when he succumbed to a sudden heart attack. One of his oldest friends said of him, " As a personal friend he was a treasure—unpretentious, kind, sincere, highly appreciative of the beautiful in nature and art and with a keen sense of humour. He was a lovable companion and one of Nature's gentlemen in the best sense." All who shared his friendship would gladly say how accurately this described him.

H. S. Raper.

ARTHUR DEHON LITTLE.

1863—1935.

ARTHUR DEHON LITTLE died at the age of 71 after a long and active life devoted to the interests of chemistry both in its academic and in its industrial aspects. It was a science he loved and during the course of his life he was able to enrich it by the full use of the ample qualities of heart and brain with which Nature had so generously endowed him. As a chemist he will be remembered because he was ever in the forefront of the march of progress and because his investigations led to an improvement in industrial conditions which is difficult of realisation excepting by those who were cognisant of chemical industrial conditions at the latter end of the last century. His visits to this country were all too few, but he was here when President of the Society of Chemical Industry and the writer has vivid recollections of the tour of the United States and Canada by the Chemical Engineers and the Society of Chemical Industry when he and his wife were able to spend many hours in the company of Dr. and Mrs. Little and to found a friendship which, despite distance, has been maintained ever since. For it is as the man rather than the chemist that he will be best remembered by those who were priviledged to know him. The kindly gentleman beloved by all and always welcome to any gathering social or scientific. His fund of stories and his genial manner made him *persona grata* to all his fellows. His loss is a sad one both to chemistry and to his friends—to the former because it could ill afford to lose his great influence on the direction of chemical matters and to the latter because he represented all that was best in the domain of human friendship.

Little was born in Boston on December 15th, 1863, and at the time of his death was Chairman of the Board of Arthur D. Little, Inc., of Cambridge (Mass.), a firm of Chemists and Engineers which he had founded with the late Roger B. Griffin forty-nine years ago. He began his professional work as chemist to the Richmond Paper Co., Rumford, R.I., the first mill in the United States to manufacture wood pulp by the sulphite process. In 1886 he opened a laboratory in Boston in partnership with R. B. Griffin to engage in the general commercial practice of chemistry, and it was at about this time that he published, in conjunction with his partner, a book on "The Chemistry of Paper Making," a treatise which for some 30 years remained the outstanding authority on the subject. Mr. Griffin was killed by an accident in 1893 and for seven years thereafter Little carried on the business alone. He formed a new partnership with Dr. William H. Walker in 1900 which continued until 1909, when the business was incorporated. In 1917 the laboratories were moved to their present position in Cambridge (Mass.).

The early years of the concern were mainly pioneering in a new and undeveloped field. Industry was antagonistic and the "technical" man was looked upon with suspicion. During those critical years it was only Little's unfailing optimism and faith in his profession that kept the path open for his future success. During that period Little took out patents of processes for the manufacture of chrome-tanned leather, chlorate of potash, and cellulose acetate and later invented processes for smoke filters, paper from southern woods, and others dealing with the recovery of naval stores from lumbering wastes. During the war he acted as consultant to the Chemical Warfare Service and the Signal Corps. He was in charge of special researches on aeroplane dopes, acetone production, smoke filters, etc., and was the inventor of the so-called "sucked-on" gas filter which became part of the standard equipment of the United States Army. Among other contributions from his laboratory are several important processes connected with pulp and paper-making, non-inflammable movie films, artificial silk, the production of alcohols, esters and other compounds from the waste gases of oil refineries, aeroplane dopes, motor-car finishes, phonograph records, and others of a widely diverse character. Truly a wonderful record and, long though his life was, it seems almost incredible that one man should have accomplished so much, and if to this is added the influence he exerted by his writings it will be realised that here, indeed, was an exceptional man.

Little was a member of the class of 1885 of the Massachusetts Institute of Technology and, as an undergraduate, had been one of the first editors of "The Tech.". His first literary production had been the book on paper-making already mentioned and as soon as

his power of expression became evident he was asked for more. The grace and dignity of his style caused him to be acknowledged as the spokesman of his profession and he became the author of many addresses delivered on special occasions when the views of chemistry required expression. His address entitled "The Fifth Estate" given at the centenary celebration of the Franklin Institute is, perhaps, the best known of these, but of equal merit are the series of articles and addresses published under the title of "The Handwriting on the Wall." He is stated to have said that his chief contribution to the welfare of his fellow men was in preaching the gospel of industrial research and it is evident that his efforts in this direction have produced results of the highest importance not only to his own country but to the industrial world at large. At the beginning of the present century industrial research was confined to practically one nation, the other nations adopting the trafficker's method of buying either the process or the finished product. The meaning of the handwriting on the wall became evident when the war broke out and parlous indeed was the position of those countries which found themselves unable to make essential materials. Little was one of those who translated the handwriting and made its meaning clear—in consequence there are few industrialists to-day who have not had their eyes opened. Such lessons are, however, soon forgotten and, after all, the methods of the trafficker are the easiest and give immediate results. Already there are indications that, in this country, we are slipping back into the old bad way; let us see to it that Little did not preach in vain.

Little was untiring in his endeavours to place chemistry on a par with the other recognised professions and urged unceasingly upon the practitioners of chemistry the importance of upholding the high standards of the profession. No one has done more for the chemical profession in America in this connexion than he has, and no inconsiderable part of the recognition and standing now accorded it both in this country and in the States is due to him.

Little was Chairman of the Advisory Committee of the National Exposition of Chemical Industries and had served as a member of the Division of Engineering and Industrial Research, National Research Council, U.S.A., as well as of the Advisory Board of Superpower Survey, U.S. Geological Survey. He was President of the Alumni Association of the Massachusetts Institute of Technology in 1921–22 and was made a life member of the Corporation of that Institution in 1923. His conception and initiation of the School of Chemical Engineering Practice at M.I.T. based on "unit operations" showed him to possess the true instincts of a "Chemical Engineer." In 1931 he was awarded the Perkin Medal as "the American chemist who has most distinguished himself by his services to applied chemistry." In 1918 the University of Pittsburgh conferred on him the honorary degree of Doctor of Chemistry and in 1929, when he was President of the Society of Chemical Industry, he was made Honorary Associate of the College of Technology, Manchester, and the University of Manchester conferred on him the honorary degree of Doctor of Science. Honorary degrees were also conferred on him by Tufts College in 1930 and by Columbia University in 1931. He was a member of many societies both in this country and in the States and served as President of the American Chemical Society, the American Institute of Chemical Engineers, and the Society of Chemical Industry.

Little died suddenly on Thursday afternoon, August 1st, at the Rock End Hotel, North-east Harbor, Maine, where he was spending the summer with Mrs. Little. He leaves a widow (formerly Henrietta Rogers Anthony), a brother, Edward H. Little of Newtownville, and a nephew, Royal Little of Providence, R.I. No better epitaph could be found for him than the citation by President Nicholas Murray Butler of Columbia University on the occasion when he received the Honorary Degree of D.Sc. "*Arthur Dehon Little, Chemical Engineer*—native of Massachusetts; a captain in the organisation and direction of research in the Science of Chemistry in all its manifold revelations; covering in his field of interest and influence almost every aspect of chemical engineering practice; fertile in invention, practical in application and a genuine leader in the preservation and advancement of that organized body of knowledge which we know as Science; one who, as even Sir Humphrey Davy would admit, pursued Science with true dignity."

J. F. THORPE.

34. *Optical Activity dependent on Co-ordinated Bivalent Ruthenium.*

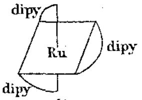
By Francis H. Burstall.

During an investigation on the action of 2 : 2′-dipyridyl (dipy) on ruthenium salts a new series of stable red salts, [Ru dipy$_3$]X$_2$,yH$_2$O, has been discovered. The *chloride* is obtained in good yield by the interaction of 2 : 2′-dipyridyl and ruthenium trichloride at 250° :

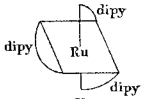
$$2RuCl_3 + 8C_{10}H_8N_2 = 2[Ru(C_{10}H_8N_2)_3]Cl_2 + C_{20}H_{14}N_4 + 2HCl$$

The base $C_{20}H_{14}N_4$ is a new tetrammine which will be the subject of a future communication. The foregoing chloride, which crystallises from water as the hexahydrate, is the starting point for the preparation of a number of salts containing the cation [Ru dipy$_3$]$^{++}$. The corresponding *bromide*, *iodide*, and *perchlorate* are all obtained by double decomposition with aqueous solutions of the chloride and they also are hexahydrates. Silver oxide, silver nitrate, and silver carbonate furnish respectively the base, *tris-2 : 2′-dipyridylruthenous hydroxide octahydrate*, [Ru dipy$_3$](OH)$_2$,8H$_2$O, the *nitrate*, [Ru dipy$_3$](NO$_3$)$_2$,6H$_2$O, and the *carbonate*, [Ru dipy$_3$]CO$_3$,6 and 10H$_2$O. The r-*tartrate* is conveniently obtained by the action of tartaric acid on the base.

These salts are appreciably more stable than the analogously constituted ferrous, [Fe dipy$_3$]X$_2$, and nickel salts, [Ni dipy$_3$]X$_2$, first prepared by Blau (*Monatsh.*, 1898, **19**, 647). Tris-2 : 2′-dipyridylferrous bromide (6H$_2$O) and iodide (5H$_2$O) were resolved into optically active forms by Werner (*Ber.*, 1912, **45**, 433), and tris-2 : 2′-dipyridylnickelous chloride (6H$_2$O) was resolved by Morgan and Burstall (J., 1931, 2213). The resolution of the tris-2 : 2′-dipyridylruthenous complex into optically active forms (I and II) has now



(I)



(II)

been accomplished. d-*Tris-2 : 2′-dipyridylruthenous* d-*tartrate* separates from an aqueous solution of the chloride and excess of ammonium *d*-tartrate, and after decomposition with aqueous potassium bromide furnishes d-*tris-2 : 2′-dipyridylruthenous bromide hexahydrate*, $[\alpha]^{25°}_{5791}$ + 860°, [*M*] + 7205°. The corresponding lævo-bromide, isolated by using *l*-ammonium tartrate, has a rotation $[\alpha]^{25°}_{5791}$ − 815°, [*M*] − 6828°. Specimens of lower rotation are obtainable from the filtrate after separation of the dextro-salt.

In comparison with the analogous iron and nickel salts the rate of racemisation of the ruthenium complexes is extremely slow. The foregoing bromides retain their activity indefinitely at room temperature not only in the solid state but also in 0·1% solution, whereas the rotations of the iron and nickel salts become negligible after about two hours in aqueous media. Moreover, *d*- and *l*-tris-2 : 2′-dipyridylruthenous bromides can be crystallised from hot water or even boiled for a few minutes without loss of optical activity. This resolution of a ruthenium compound is the first in which the metal is contained in a complex cation; activity due to a co-ordinated ruthenium anion has, however, been recorded by Charonnat (*Ann. Chim.*, 1931, **16**, 126), who obtained *d*- and *l*-forms of the complex salts R[Ru(NO)(C$_5$H$_5$N)(C$_2$O$_4$)$_2$] (R = NH$_4$ and C$_5$H$_6$N).

Tris-2 : 2′-dipyridylruthenous salts dye silk and wool in orange-yellow shades.

Experimental.

Tris-2 : 2′-dipyridylruthenous Chloride Hexahydrate.—Ruthenium trichloride (6·0 g.) and 2 : 2′-dipyridyl (50 g.) were stirred and slowly heated; reaction started at 250°, the temperature rose to 260°, and the black ruthenium trichloride became dark brown and crystalline, the change being accompanied by a considerable increase in the quantity of insoluble product. The mixture was stirred at 250—260° for 3 hours; the cooled melt was then extracted with hot

benzene until no more solid dissolved. The yellow-brown residue (17 g.) was dissolved in water, filtered from insoluble material, including a little ruthenium, and evaporated to crystallising point. The bright red leaflets were collected, recrystallised from a small quantity of hot water, and dried over sulphuric acid (Found : C, 48·4; H, 4·6; N, 11·35, 11·3; Cl, 10·1, 9·9; Ru, 13·5, 13·4; H_2O, 14·2. $[C_{30}H_{24}N_6Ru]Cl_2,6H_2O$ requires C, 48·1; H, 4·8; N, 11·2; Cl, 9·5; Ru, 13·6; H_2O, 14·4%). The complex chloride was also formed by the action of 2 : 2′-dipyridyl on (a) ruthenium trichloride in an aqueous or alcoholic medium, (b) chlorotetramminohydroxyruthenium chloride hydrate (ruthenium-red) at 250° or in aqueous solution, (c) potassium nitrosoruthenium pentachloride at 250° or on prolonged action in an aqueous medium, (d) neutral salts of the types $R_2[RuCl_6]$ and $R_2[RuCl_5]$ or $R[RuCl_4]$. These preparations did not give such good yields as the method described above. *Tris-2 : 2′-dipyridylruthenous chloride hexahydrate* forms well-defined, bright red leaflets easily soluble in water and alcohol, but insoluble in acetone, chloroform, benzene, and petroleum. Slow crystallisation gave large, deep ruby-red rhombs. The chloride was unchanged by boiling concentrated hydrochloric acid or 50% caustic alkali. Concentrated sulphuric acid gave an orange-yellow solution, which became green on warming, and concentrated nitric acid furnished a deep green solution. Hydrogen peroxide and chlorine were without action at room temperature. Water of crystallisation was eliminated at 200° in a vacuum, but the salt was not decomposed below 300°.

Tris-2 : 2′-dipyridylruthenous Bromide Hexahydrate.—(a) An aqueous solution of the foregoing chloride was treated with excess of a concentrated solution of potassium bromide. (b) A solution of the base (*vide infra*) was treated with hydrobromic acid. The pink leaflets were crystallised from water (Found: Ru, 12·3; Br, 19·6; N, 10·2. $[C_{30}H_{24}N_6Ru]Br_2,6H_2O$ requires Ru, 12·1; Br, 19·1; N, 10·0%).

Tris-2 : 2′-dipyridylruthenous Iodide Hexahydrate.—Concentrated aqueous solutions of the chloride and potassium iodide were mixed. The red crystalline precipitate was recrystallised from hot water (Found : Ru, 11·2; I, 27·6; N, 9·1. $[C_{30}H_{24}N_6Ru]I_2,6H_2O$ requires Ru, 10·9; I, 27·2; N, 9·0%).

Tris-2 : 2′-dipyridylruthenous Perchlorate Hexahydrate.—(a) Concentrated aqueous solutions of sodium perchlorate and the complex chloride were mixed. (b) Perchloric acid was added to a solution of the base (*vide infra*). The sparingly soluble salt was crystallised from water {Found : Ru, 11·5; ClO_4, 22·2. $[C_{30}H_{24}N_6Ru](ClO_4)_2,6H_2O$ requires Ru, 11·6; ClO_4, 22·7%}.

Tris-2 : 2′-dipyridylruthenous Nitrate Hexahydrate.—Aqueous solutions containing equivalent quantities of the complex chloride or bromide (1 mol.) and silver nitrate (2 mols.) were mixed. The heated solution was filtered from silver halide and concentrated to crystallisation point. The red leaflets, which were readily soluble in water and alcohol, showed no signs of tervalent ruthenium {Found : Ru, 12·6; N, 14·2. $[C_{30}H_{24}N_6Ru](NO_3)_2,6H_2O$ requires Ru, 12·7; N, 14·0%}.

Tris-2 : 2′-dipyridylruthenous Hydroxide Octahydrate.—A concentrated aqueous solution of the foregoing chloride or bromide was shaken with an excess of freshly prepared silver oxide until it was free from halogen. The orange-red filtrate from the silver halide was evaporated to dryness over caustic soda. The complex *base* was recrystallised by cooling a solution in a small quantity of hot water to 0°, and dried over caustic potash {Found : Ru, 13·5; N, 11·3. $[C_{30}H_{24}N_6Ru](OH)_2,8H_2O$ requires Ru, 13·6; N, 11·2%}. This stable but rather hygroscopic base displaced ammonia from ammonium salts, precipitated metallic oxides or hydroxides from solutions of heavy-metal salts, and formed a carbonate with carbon dioxide.

Tris-2 : 2′-dipyridylruthenous Carbonate Decahydrate.—(a) An aqueous solution of the complex chloride or bromide was shaken with freshly prepared silver carbonate. (b) Carbon dioxide was passed into a solution of the foregoing base. The complex *carbonate* crystallised from cold concentrated solutions in red leaflets and was air-dried (Found : Ru, 12·5; N, 10·8. $[C_{30}H_{24}N_6Ru]CO_3,10H_2O$ requires Ru, 12·5; N, 10·4%). Four molecules of the water of crystallisation were lost over sulphuric acid in a vacuum (Found : loss, 9·2. Calc. for $4H_2O$, 8·9%).

Tris-2 : 2′-dipyridylruthenous Tartrate Hexahydrate.—Aqueous solutions containing equivalent quantities of the complex base and tartaric acid were mixed and evaporated to crystallising point. The very soluble *tartrate* was dried over sulphuric acid (Found : Ru, 12·6; N, 10·5. $[C_{30}H_{24}N_6Ru]C_4H_4O_6,6H_2O$ requires Ru, 12·3; N, 10·2%). It was also obtained from ammonium tartrate and the complex chloride in aqueous solution.

Optical Resolution of Complex Ruthenium Salts.—d-*Tris-2 : 2′-dipyridylruthenous* d-*tartrate hexahydrate.* Tris-2 : 2′-dipyridylruthenous chloride hexahydrate (2·5 g.) in water (100 c.c.) was cooled to 0°, and ammonium *d*-tartrate (50 g.) added all at once to the mechanically stirred

solution. Small red crystals of the complex tartrate soon appeared and after 60 minutes the mixture was decanted from undissolved ammonium *d*-tartrate and filtered, and the complex tartrate dried on a porous plate. A 0·1% solution gave α + 0·73°; $[\alpha]^{25°}_{5791}$ + 365° (l = 2 dm.).

d-*Tris*-2 : 2′-*dipyridylruthenous bromide hexahydrate.* The foregoing active tartrate was dissolved in water and excess of concentrated aqueous potassium bromide added. The active bromide separated in small red plates; it was recrystallised from warm water until no further increase in optical rotation was noted. The final value for a 0·1% solution (l = 2) was α + 1·73°; $[\alpha]^{25°}_{5791}$ + 860°, whence $[M]$ + 7205°. The active bromide separated as the least soluble fraction in the crystallisations (Found: Ru, 12·6. Calc.: Ru, 12·1%). It remained unchanged in activity at room temperature, but racemised slowly at 90°. The rotation was not altered appreciably after conversion of the bromide into the complex carbonate by silver carbonate.

l-*Tris*-2 : 2′-*dipyridylruthenous bromide hexahydrate* was prepared in a similar manner to the dextrorotatory bromide, ammonium *l*-tartrate being used instead of the *d*-salt. After several crystallisations a 0·1% solution (l = 2) gave α − 1·63°, $[\alpha]^{25°}_{5791}$ − 815°; whence $[M]$ −6828°.

Treatment of the filtrate from *d*-tris-2 : 2′-dipyridylruthenous *d*-tartrate with potassium bromide precipitated the lævorotatory bromide, α − 0·45°, $[\alpha]^{25°}_{5791}$ − 225°, but the product was not sufficiently active for repeated crystallisation to lead to a pure specimen.

The author thanks the Mond Nickel Co. for a loan of ruthenium and Professor G. T. Morgan, F.R.S., for his kindly interest and permission to publish the results.

CHEMICAL RESEARCH LABORATORY, TEDDINGTON, MIDDLESEX. [*Received, November* 30*th*, 1935.]

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35. *Stereochemistry of Some New Complex Thio-salts of Mercury, Cadmium, and Zinc.*

By WILLIAM H. MILLS and ROBERT E. D. CLARK.

THE general stability of the sulphur compounds of the heavy metals, and the power shown by mercury and allied elements of forming 4-co-ordination sulphur compounds like the mercuri- and zinci-thiocyanates, $K_2M''(SCN)_4$ (M″ = Hg or Zn), gave reason to suppose that benzene-1 : 2-dithiols might yield stable co-ordination derivatives of mercury and similar metals of the general formula (I) (M′ = alkali metal). Spirocyclic metallic compounds of this type would, if suitably substituted, provide a means of investigating the stereochemistry of the metals (in the 4-covalent state) from which they were derived.

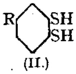
With the object, therefore, of obtaining molecularly dissymmetric metallic derivatives of this kind, we undertook the preparation of *o*-dithiolbenzenes containing an additional substituent group. The preparation of *o*-dithiolbenzene itself has been described by Pollak (*Monatsh.*, 1913, **34**, 1673) and by Hartley and Smiles (J., 1926, 1821), and we prepared the substitution derivatives of the type required by analogous methods. We obtained *toluene*-3 : 4-*dithiol* (II; R = Me) and 1-*chlorobenzene*-3 : 4-*dithiol* (II; R = Cl)

$$\left[C_6H_4{<}^{S}_{S}{>}M''{<}^{S}_{S}{>}C_6H_4\right]M'_2$$

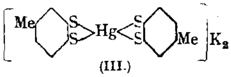
(I.)

$$\left[C_6H_3Cl{<}^{S}_{S}{>}Hg{<}^{S}_{S}{>}C_6H_3Cl\right](\text{Quinine, H})_2$$

(IV.)



(II.)



(III.)

by reducing the chlorides of the corresponding *o*-disulphonic acids, and found that these substituted *o*-dithiols did, in fact, give rise to complex salts of mercury, cadmium, and zinc of the type contemplated. For instance, when an alcoholic solution of the monopotassium salt of (I; R = Me) was heated with mercuric oxide, the crystalline *potassium* salt (III) was produced, and salts of the analogous zinc and cadmium complex acids could be prepared in the corresponding manner.

Various crystalline alkaloid salts of these acids were investigated, but in no case could

direct evidence of their optical resolution be obtained. However, the *quinine* salt (IV) of the spirocyclic mercuric complex acid derived from the chloro-dithiol (II; R = Cl) was found to show a highly characteristic behaviour. It exists in two forms, interconvertible in a remarkable way. When prepared by heating equimolecular quantities of the dithiol and quinine in chloroform solution with mercuric oxide, the α-modification is formed. This is sparingly soluble in chloroform but it dissolves very easily in acetone, and the resulting solution within a few seconds begins to deposit the salt in a new form, the β-form, which is sparingly soluble in acetone and shows great crystallising power. This β-form shows the converse behaviour. It dissolves rapidly in cold chloroform, and the solution then sets to a jelly, which on keeping at 40—60° for some time crystallises, yielding the α-form. The interconversion of the two forms in this way can be repeated indefinitely.

↗ acetone solution ↘
α-form ↖ ↙ β-form
chloroform solution

The corresponding *zinc* and *cadmium* compounds behave in an exactly similar manner. Their quinine salts each exist in two forms, which are intertransformable by means of acetone and chloroform, and the process is even more rapid than with the mercury compound.

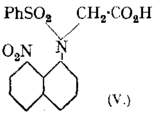
Both the α- and the β-forms of these salts crystallise with solvent of crystallisation, but the solvent is very loosely bound, and the crystals effloresce on exposure to air, yielding cream-coloured powders.

In the desolvated powders, the crystal-lattices of the solvated salts must have been destroyed, but the α- and β-modifications still retain their individuality, since the desolvated α-powders, like the α-crystals, dissolve easily in acetone but not in chloroform, and the β-powders show the converse behaviour. Also, the β- differ from the α-powders in being conspicuously triboelectric: a similar distinction was observed by Angel, Drew, and Wardlaw (J., 1930, 357) between α- and β-modifications of the halides of bis(diethyl-sulphide)platinum.

There must, therefore, be a real molecular difference between the two forms. They cannot be merely crystalline modifications produced by the crystallisation of the same molecular species in different lattices.

Acetone and chloroform are not the only solvents by which the transformation can be effected. The α-forms dissolve in methyl ethyl ketone and, in the cases of the cadmium and the zinc complexes, the β-forms separate on standing (the mercuric compound is too soluble). The β-forms are soluble in methylene chloride, giving solutions which, like the chloroform solutions, set to jellies passing over into the crystalline α-forms when kept warm.

The convertibility of these salts into different modifications by treatment with solvents recalls a similar phenomenon encountered by Mills and Elliott (J., 1928, 1291) with the brucine salt of benzenesulphonyl-8-nitro-1-naphthylglycine (V). The salt of the *l*-form of this acid dissolved easily in cold methyl alcohol, and from the solution, after a short interval, the salt of the *d*-acid crystallised (as a dihydrate). The latter salt was easily soluble in cold acetone, and this solution rapidly deposited the brucine salt of the *l*-acid. In this case it could be proved that the behaviour was due to the presence in the salt of a molecularly dissymmetric anion which underwent rapid autoracemisation. It is probable that the analogous behaviour of the quinine salts of these spirocyclic metallic complexes is to be referred to a similar cause.



(V.)

If the four sulphur atoms in the complex anion are arranged tetrahedrally round the central metallic atom, the anion is dissymmetric and will exist in enantiomorphous *d*- and *l*-forms. It will then give two quinine salts, *viz.*, *l*B,*d*A and *l*B,*l*A. If, of these two diastereoisomeric salts, one is considerably the more soluble in chloroform and the other in acetone, and if, further, the anion undergoes rapid autoracemisation in solution, then an intertransformation corresponding with that observed will result.

The rapidity with which interconversion of the α- and β-forms takes place would indicate that, if this view of the inter-relationship of the two forms is correct, the rate of racemisation

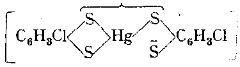
of the optically active complexes must be very high. It was therefore unlikely that their optical activity would be sufficiently persistent to be observable after removal of the quinine, and solutions of the sodium salts, prepared by the addition of sodium hydroxide to either form and extraction of the alkaloid with chloroform, were in fact inactive.

It seemed, however, that it might not prove impossible to observe the oppositely directed mutarotations of the two forms that should be caused by the passage of the optically active anions into the *dl*-equilibrium mixture when the crystalline salts passed into solution.

No mutarotation could be detected at 0°. A silica apparatus (see fig.) was therefore constructed which enabled solutions to be examined at temperatures down to − 35° and polarimetric readings to be taken, sometimes within 20 seconds of bringing the solid salt into contact with the solvent. Solutions of the α-forms of the quinine salts in acetone and also in methyl ethyl ketone, and of the β-forms in chloroform and in methylene chloride, were examined, but even under the lowest practicable temperatures and with the greatest rapidity of working which we could attain, no mutarotation could be observed. It cannot be concluded from this, however, that mutarotation does not occur. A time of the order of ½ minute is enormously long in comparison with the periods of molecular vibrations, and mutarotation may well have occurred and proceeded to completion before our polarimetric observations on the solutions could begin.

It is difficult to find a satisfactory alternative to the view that the isomerism is diastereoisomerism due to the dissymmetry of the complex acids. If the valencies of the central metallic atom had a uniplanar distribution, geometrical isomerism dependent on the *cis-* or *trans*-arrangement of the unsymmetrically substituted phenylene groups would be possible, but a valency arrangement of this kind is improbable, since *X*-ray examination of the complex cyanides of potassium with zinc, cadmium, and mercury of the type $K_2[X(CN)_4]$—in which an analogous configuration of the anion is to be expected—has indicated a tetrahedral arrangement of the co-ordinated cyanogen groups round the central metallic atom (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 774). Moreover, the isomerism would then be independent of the dissymmetry of the base and should be shown also by metallic salts of the complexes.

It also seems improbable that the isomerism is structural, dependent on an internal dissociation of the spirocyclic salt, analogous to the dissociation of the mercuritetrathiocyanate ion into the mercuritrithiocyanate and the thiocyanate ion: $Hg(SCN)''_4 \rightleftharpoons Hg(SCN)'_3 + SCN'$. On this view, one form would possess the normal spirocyclic structure (IV) and the other would have a formula (VI) with 3-co-ordinated mercury and an ionised thiol group. It is to be observed, however, that the dissociation of the mercuri-


$(Quinine, H^+)_2$ (VI.)

tetrathiocyanate ion occurs to an appreciable extent only at high dilutions (Grossmann, *Z. anorg. Chem.*, 1905, **43**, 369), whilst in a compound of formula (VI) the mercury and sulphur would be held in relative positions corresponding with the very highest concentrations.

This view of the isomerism would require that the salts of the complex anion should exist in solution as equilibrium mixtures of the spirocyclic and internally dissociated forms, so that one or the other could crystallise according to the solvent employed. Alcoholic or chloroform solutions of the mercuric compound can, however, contain no appreciable amount of an internally dissociated modification, since these solutions do not react with mercuric oxide, as they should if the ionised thiol group Ar-$\bar{S}$ was present, to form a mercaptide linking Ar-S-Hg- (Ar representing the aromatic group contained in these compounds). This is shown by the fact that when alcoholic solutions of the potassium salts, or chloroform solutions of the alkaloidal salts, of the dithiols are brought into contact with mercuric oxide, the oxide dissolves until the amount required to form the 4-co-ordination derivative has been taken up, and then the action ceases.

The corresponding test cannot be made with acetone solutions, as acetone itself reacts with mercuric oxide. It is conceivable that solvation by acetone of the 3-co-ordinated mercury atom or of the ionised thiol group might make the proportion of the internally dissociated form higher in this than in other solvents, but the acetone is loosely bound in the crystalline β-forms, and on its removal these forms show no tendency to pass into the isomeric α-modifications.

Hence, although in the absence of evidence of optical activity, the interpretation of the isomerism of these quinine salts as diastereoisomerism due to the dissymmetry of the spirocyclic complex acids from which they are derived has not been proved, it is the most probable of the explanations which we are able to suggest, and it is strongly supported by the analogous behaviour of the brucine salt of benzenesulphonylnitronaphthylglycine.

EXPERIMENTAL.

Toluene-3 : 4-*disulphonyl Chloride*.—Powdered sodium toluene-3 : 4-disulphonate (14·8 g.) was refluxed for 4 hours with phosphorus pentachloride (21 g.) and oxychloride (10 c.c.). The mixture was poured on ice, and the oil solidified (9·9 g.); recrystallised from light petroleum (b. p. 80—100°), it had m. p. 109° (Found : Cl, 24·3; S, 22·2. Calc. for $C_7H_6S_2O_4Cl_2$: Cl,24·6; S, 22·15%) (compare Klason, *Ber.*, 1887, **20**, 356; Wynne and Bruce, J., 1898, **73**, 751).

Toluene-3 : 4-*dithiol*.—The above sulphonyl chloride (45 g.) was reduced by boiling with tin (350 g.) and hydrochloric acid (1000 c.c.). After 20 minutes, the flask was rapidly cooled, and benzene (150 c.c.) added, the mixture being immediately filtered (temperature about 40°). The aqueous layer was again extracted with benzene after separation, and the combined benzene extracts dried with sodium sulphate. The benzene was removed, and the residual oil distilled in a vacuum; b. p. 185—187°/84 mm., 174°/41 mm. The colourless oil crystallised readily; m. p. 35°, yield 37·4 g. (79%) (Found : C, 53·8; H, 5·1; S, 40·4. $C_7H_8S_2$ requires C, 53·9; H, 5·1; S, 41·0%).

p-*Chloroanilinesulphonic Acid*.—The following method, based on Fries's (*Annalen*, 1895, **286**, 377) preparation of the bromo-derivative, was employed. *p*-Chloroacetanilide (52 g.) and concentrated sulphuric acid (30 g.) were heated in a dish and stirred with a thermometer. Acetic acid boiled off at 140—190°, at which temperature the mass suddenly became solid. It was kept at 180° for 1—2 hours and recrystallised from water (charcoal); yield 43—45 g. (Found, by titration : equiv., 206·5. Calc. : 207·5).

1-*Chlorobenzene*-3 : 4-*disulphonyl Chloride*.—*p*-Chloroanilinesulphonic acid in lots of 83 g. was dissolved in sodium hydroxide (400 c.c. of *N*, with 500 c.c. of water), and the solution added to ice (1 kg.) and hydrochloric acid (200 c.c.). The finely divided acid thus precipitated readily dissolved when sodium nitrite (30 g.) was sifted in. After being stirred for ½ hour, the mixture was neutralised by addition of sodium bicarbonate (159 g.), and 100 g. of potassium xanthate in 100 c.c. of water were run in. The liquid was warmed to decompose the diazonium xanthate, evaporated to dryness, and the residue extracted with alcohol. After removal of alcohol, the residue was oxidised with nitric acid (*d* 1·4; 240 c.c. for the product from each lot of 83 g. of chloroanilinesulphonic acid). The oxidation can be carried out on the combined products of several operations. After removal of nitric acid on the water-bath, barium chloride (200 g. per 83 g. of original acid) was added, and the crude *barium* salt thus precipitated (Found : Ba, 33·8. $C_6H_3O_6ClS_2Ba$ requires Ba, 33·7%) was then treated with sodium sulphate, the resulting sodium salt being obtained by evaporation. This was treated with phosphorus pentachloride (250 g. per 170 g. of sodium salt), and the reaction mixture poured on to ice after being heated for 3 hours at 140°. The crude *sulphonyl chloride* was crystallised from benzene as rapidly as possible, the product washed with petrol, and dried; yield 800 g. from 1594 g. of sodium salt. Recrystallised from a large volume of light petroleum (b. p. 100—120°), it gave colourless crystals, m. p. 82—83° (Found : C, 23·4; H, 1·1; Cl, 34·6; S, 20·7. $C_6H_3O_4Cl_3S_2$ requires C, 23·3; H, 1·0; Cl, 34·4; S, 20·7%).

1-*Chlorobenzene*-3 : 4-*dithiol*.—The above sulphonyl chloride (150 g.) was reduced with tin (500 g.) and hydrochloric acid (1·2 l.) by boiling until nearly all the tin had dissolved. The flask was plunged in ice-water with vigorous shaking until the temperature was reduced to 70°; benzene (200 c.c.) was then added, and the strongly vesicant liquid filtered rapidly. The mother-liquor was extracted once with benzene (50 c.c.) after separation. The benzene was distilled off after drying with sodium sulphate and reserved for subsequent preparations. The residual oil distilled at 165°/32·5 mm., giving a colourless liquid which crystallised on standing;

m. p. 31° (Found: C, 40·8; H, 2·9; Cl, 19·9; S, 36·8. $C_6H_5ClS_2$ requires C, 40·8; H, 2·8; Cl, 20·1; S, 36·3%). The yield varied from 40 to 65 g., since no method of avoiding the formation of the red tin compound could be relied upon. The red compound, obtained as a by-product when the yield was low, was decomposed by boiling with hydrochloric acid and then worked up as above.

Dipotassium Bis(toluene-3 : 4-dithiol)mercury (III).—Potassium (3·22 g.) was dissolved in absolute alcohol (80 c.c.), and toluene-3 : 4-dithiol (13·1 g.) added. Yellow mercuric oxide (9·0 g.) was then added, and the mixture refluxed for 20 minutes. The oxide dissolved, and, on cooling, the colourless highly crystalline *potassium* salt separated (13·0 g.); it was washed with a little absolute alcohol and air-dried. The mother-liquor deposited another 5·3 g. on addition of anhydrous ether. Total yield, 17·8 g. (72%) (Found: C, 30·4; H, 3·6; K, 12·5; Hg, 32·0; EtOH, 7·4. $C_{14}H_{12}S_4K_2Hg,C_2H_6O$ requires C, 30·3; H, 2·8; K, 12·3; Hg, 31·6; EtOH, 7·3%). On heating to 100—110° for 1—2 hours, or on prolonged standing in a desiccator, the alcohol-free substance was obtained as a faint yellow powder, easily soluble in water and alcohol (Found: C, 28·6; H, 2·6; S, 21·9; K, 13·5. $C_{14}H_{12}S_4K_2Hg$ requires C, 28·7; H, 2·05; S, 21·8; K, 13·3%). The aqueous solution slowly decomposed, depositing the mercury mercaptide, but the solution was stable to carbon dioxide. The potassium salt was very soluble in alcohol containing a small quantity of water, and filtrations had to be performed out of contact with moist air.

When cadmium hydroxide was used in the above preparation, addition of ether afforded a gum, which passed on standing into large, highly hygroscopic crystals having the expected properties of the quinine–cadmium salt. Zinc oxide gave a high yield of a quinine–zinc salt which readily crystallised from alcohol.

Alkaloidal Salts.—Alkaloidal salts were prepared (1) by interaction of dipotassium salts with the hydrochloride or sulphate of the base dissolved in alcohol, and (2) directly from mercuric oxide (1 mol.) with a chloroform solution of the base (2 mols.) and the thiol (2 mols.). The products appeared to be identical. Brucine, strychnine, quinine, cinchonine, morphine, nor-*d*-ψ-ephedrine, methylstrychnidinium, methylbrucidinium, and bromostrychnine salts of the mercury complex were prepared, but none crystallised except the last-named. Beautifully crystalline quinine salts of the zinc and cadmium complexes were prepared, but no evidence of resolution could be obtained.

Diquinine Dihydrogen Bis-(1-chlorobenzene-3 : 4-dithiol)mercury.—Quinine (13·0 g.) and 1-chlorobenzene-3 : 4-dithiol (7·1 g.) were dissolved in chloroform (80 c.c., free from carbonyl chloride), and mercuric oxide (4·4 g.) added. The latter dissolved, generating sufficient heat to boil the liquid. The mixture was refluxed until, after 5—10 minutes, it set to a jelly. The flask was then placed in a water-bath at 55—65° for 2 hours, the jelly then crystallising. The crude product (25·0 g.) was removed by filtration and washed with chloroform. It was then dried in a steam-oven until most of the chloroform was removed (*ca.* 15 mins.), but on no account longer.

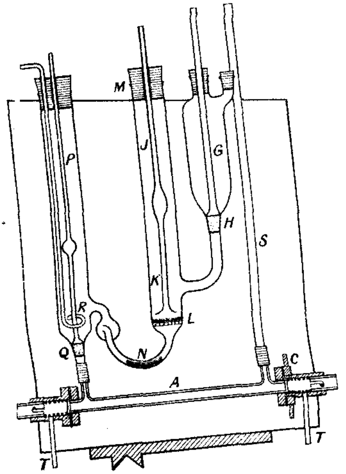
β-Form. Small portions (1—2 g.) of the above crude α-form were placed in a flask, and acetone (not less than 15 c.c.) added. The flask was immediately plunged into boiling water for 4 seconds, and the liquid then instantly filtered at the pump. The acetone solution deposited the *β-form* (15·5 g. from 25 g. crude), which was removed by filtration in ½—¾ hour, and washed with acetone. The colourless crystals were dried at 100° and gave a cream-coloured powder, m. p. 138° (Found: Cl, 5·6; S, 11·3; Hg, 16·7; Quinine, 53·6. $C_{12}H_6Cl_2S_4Hg,2C_{20}H_{24}O_2N_2$ requires Cl, 5·9; S, 10·7; Hg, 16·7; Quinine, 54·0%).

α-Form. 23·5 G. of the β-form (above) were treated in quantities of 4·0 g. with 25 c.c. of chloroform, plunged into boiling water (3 secs.), and filtered rapidly.* The filtrate set to a jelly. This was kept at 60° for 2 hours, and the crystalline product filtered off hot and washed with chloroform; yield, 16·5 g. after drying at 100°. The filtrate on evaporation gave a gum which in acetone deposited the β-form (3·2 g.). The *α-form* had m. p. 142° to a viscons yellow liquid. It dissolved immediately in cold acetone, depositing the β-form in 90% yield (Found: Cl, 5·8; S, 11·1; Hg, 17·2; Quinine, 53·2%). Specific rotations: α-form (in acetone; $c = 0{\cdot}93$; $l = 2$), $\alpha_{5461}^{15^\circ} = -3{\cdot}38^\circ$; whence $[\alpha]_{5461}^{15^\circ} = -182^\circ$; β-form (in chloroform; $c = 0{\cdot}502$; $l = 2$), $\alpha_{5461}^{17^\circ} = -2{\cdot}41^\circ$; whence $[\alpha]_{5461}^{17^\circ} = -240^\circ$. In order to compare the rotations of the two

* The β-form dissolves in chloroform at once at the ordinary temperature, but at 0° a small quantity persists in the form of a fine suspension for a few seconds. At still lower temperatures the suspension may remain undissolved for a considerable time. The same phenomenon is to be observed with the zinc and cadmium complexes.

forms in the same solvent, the α-form was dissolved in acetone and an equal volume of chloroform added, and the β-form was dissolved in chloroform and an equal volume of acetone added. For $c = 1$ the values found were: α-form, $[\alpha]_{5461}^{20°}$ − 191°; β-form, $[\alpha]_{5461}^{20°}$ − 188°. These may be taken as identical within the limits of experimental error, for it was more difficult to obtain rapid solution of the β-form.

Diquinine Dihydrogen Bis-(1-chlorobenzene-3 : 4-dithiol)cadmium.—β-*Form.* The chlorothiol (7·1 g.), quinine (13·0 g.), and cadmium hydroxide (3·2 g.; calc., 3·0 g.) were boiled with chloroform (80 c.c.). The hydroxide dissolved with little heat evolution. When the mixture set to a solid mass, it was removed to a bath at 60° and kept there for 2 hours to crystallise; crude yield, 22 g. This substance (15 g.) was converted into the β-form (9·6 g.) by treating it in quantities of 4 g. with acetone (22 c.c.) as described in the case of the mercury compound. The pure β-*form* (obtained by converting this product into the α-form and back again) had m. p. 157° (Found: N, 4·8; Cl, 6·5; Cd, 9·8; Quinine, 57·2. $C_{12}H_8Cl_2S_4Cd,2C_{20}H_{24}O_2N_2$ requires N, 5·0; Cl, 6·4; Cd, 10·1; Quinine, 58·3%).



α-*Form.* The β-form (4·0 g.) was treated with chloroform (30 c.c.), plunged into boiling water (4 secs.), and filtered at the pump. The liquid set to a jelly far more rapidly than in the case of the mercury analogue. It became crystalline on keeping at 60° for 2 hours. It was filtered off hot and washed with chloroform; yield, 7·5—8·0 g., from 9·5 g. of β-form. Unlike the mercury compound, the air-dried material contained *chloroform of crystallisation* which had partly effloresced. When dried, the product always gave high values for chlorine, but it was finally obtained pure (Found: Cl, 6·5; Cd, 9·8%) by employing methylene chloride instead of chloroform in the above preparation.

Diquinine Dihydrogen Bis(toluene-3 : 4-dithiol)zinc. — α-*Form.* Quinine (13·0 g.) and toluene-3 : 4-dithiol (7·1 g.) in chloroform (70 c.c.) were treated with zinc oxide (1·9 g.; calc., 1·7 g.) which dissolved without appreciable heat evolution. On boiling, the liquid rapidly set to a solid (3—5 mins.). It was kept at 60° for an hour, and the crystals which formed were filtered off (after addition of 20 c.c. more chloroform) and dried (21 g.). The crude compound dissolved immediately in cold acetone, but the β-form separated so rapidly that filtration was impossible. Purification was effected as follows. Portions of the above crude product (4·0 g.) were dissolved by boiling with 60 c.c. of acetone–chloroform (1 : 1 by vol.), and filtered quickly. On cooling, the original α-*form* (13·0 g., from 21 g. crude) separated; m. p. 155°. It was free from chloroform of crystallisation (Found, in air-dried substance: Cl, 6·8; S, 11·7; Zn, 6·1; Quinine, 60·3. $C_{12}H_8Cl_2S_4Zn,2C_{20}H_{24}O_2N_2$ requires Cl, 6·8; S, 12·3; Zn, 6·3; Quinine, 60·1%).

β-*Form.* The above α-form, in lots of 2 g., was treated with acetone (15 c.c.), which quickly dissolved it, giving a completely clear solution. The β-*form* separated rapidly (1·7 g. per 2·0 g. of α-form). This was filtered off and washed with acetone; m. p. 145° (sintering at 128°) (Found: Cl, 6·7; Zn, 5·9; Quinine, 60·9%).

Apparatus for Rapid Low-temperature Polarimetry.

The apparatus (see fig.) consists of three vertical containers, *G*, *J*, and *P*, held in a metal tank for the cooling liquid and connected with the 2-dcm. observation tube *A*. The tank is

fixed on the stand of the polarimeter so that A is correctly placed between the polariser and analyser of the polarimeter, which is tilted so that the top of the tank is horizontal.

The solvent is stored in G and allowed to attain the temperature of the bath.* By temporarily raising the stopper H it is then admitted to J, which is fitted at the bottom with a filter L on which the substance to be examined is placed. Solution of the substance is promoted by means of the stirrer K which has a tubular stem. The upper end of K is connected, through a rubber tube closed with a clip, to a reservoir of air under pressure.

When the substance has dissolved, the stirrer K is raised until the bulb on its stem closes the boring in the rubber stopper M. The clip is then opened and the solution, which till now has been prevented from passing the filter by the back pressure of the mercury column N, is driven through into P. Here it is rendered homogeneous by a few strokes of the stirrer R, which is then raised till it lifts the stopper Q by engaging with the bulb on its stem, and the solution flows into the slightly inclined observation tube A, the displaced air escaping through S.

The observation tube is held in the tank by pressure applied by the screw C to rubber washers bearing on brass flanges cemented on to the ends of the tube. The end-plates are held in position by spiral springs secured externally by tubes kept in position by bayonet-catches. The condensation of moisture on the end-plates is prevented by a current of dry air admitted by the tubes TT.

Our thanks are due to the Department of Scientific and Industrial Research for a grant.

University Chemical Laboratory, Cambridge. [*Received, September 27th*, 1935.]

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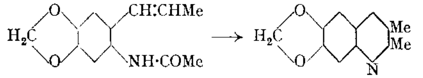
36. *Ring Closures of Derivatives of 2-Aminostyrene.*

By T. W. J. Taylor and (Miss) P. M. Hobson.

Foulds and Robinson (J., 1914, **105**, 1968) obtained methylenedioxydimethylquinoline (II) by boiling 2-acetamidosafrole (I) with phosphoryl chloride.

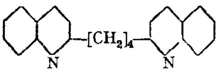
(I.)  (II.)

The purpose of the experiments recorded here was to see whether this type of quinoline synthesis could be extended to the acyl derivatives of 2-aminostyrene (V; R = H, R′ = acyl) and 2-aminostilbene (V; R = Ph, R′ = acyl). 2-Aminostyrene can be obtained from β-phenylethyl acetate (Sabetay, Bléger, and De Lestrange, *Bull. Soc. chim.*, 1931, **49**, 3), but the process is tedious and the yield small because the nitration gives mainly the 4-nitro-compound. Attempts to prepare the desired substance by other methods were unsuccessful. 2-Nitrocinnamic acid could not be decarboxylated to 2-nitrostyrene under any of the conditions or with any of the catalysts which were tried. β-2 : 4-Dinitrophenylethyl acetate, from which the 4-nitro-group might be eliminated, could not be obtained by the nitration of β-4-nitrophenylethyl acetate, only side-chain oxidation products being isolated. Blocking of the 4-position in phenylethyl acetate with a bromine atom did not prove a suitable method for increasing the amount of the 2-nitro-compound formed in nitration, since 4-bromophenylethyl acetate cannot be prepared by direct bromination.

It was found that the acyl derivatives of 2-aminostyrene can be converted into 2-substituted quinolines by heating with phosphoryl chloride, and in this way quinaldine was obtained from the acetyl compound, 2-*n*-amylquinoline from the *hexoic* derivative, and *αδ-di-(2-quinolyl)butane* (III) from *adipodi-2-vinylanilide*. This type of quinoline synthesis may prove useful for obtaining certain quinoline derivatives not accessible by other methods. 2-Aminostyrene can also be converted into indole; addition of bromine

* An aqueous solution of calcium chloride kept at its freezing point by the occasional addition of commercial solid carbon dioxide.

to the acetyl compound gives the dibromide (IV), from which indole is obtained with alcoholic potash (cf. Foulds and Robinson, *loc. cit.*).



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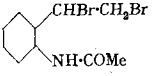
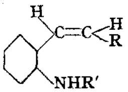
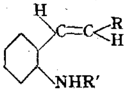


(IV.)

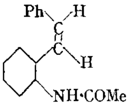


(V.)

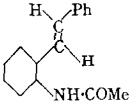


(VI.)

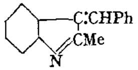
No quinoline derivatives could, however, be obtained from 2-acetamidostilbene. This compound should exist in two geometrically isomeric forms, of which only the *trans*-compound (VI; R = Ph, R′ = Ac) could give a quinoline, since in the *cis*-form (V) the hydrogen atom which would be involved in the ring closure is on the wrong side of the double bond.



(VII.)



(VIII.)



(IX.)

The two isomerides have been obtained and their configurations established, as is discussed below. With the *cis*-acetamido-compound, ring closure gives 3-benzylidene-2-methylindolenine (IX); this result would be expected, since, although a quinoline cannot be formed, the molecule can exist as in (VII) and a five-membered ring can be formed. The *trans*-compound undergoes the same ring closure as the *cis*-compound and gives no quinoline, in spite of the fact that its spatial configuration does not exclude that possibility. It is clearly reacting in the form (VIII) and the introduction of the phenyl group has upset the balance between quinoline and indole formation.

The aminostilbenes were prepared from *cis*-2-nitrostilbene, which has been obtained pure and in good yield. The behaviour of this compound is exceptional (cf. Stoermer and Prigge, *Annalen*, 1915, **409**, 34) in that it cannot be converted into the *trans*-isomeride by the methods which are effective for other *cis*-stilbenes. This behaviour seems to arise from the presence of the nitro-group, since it is also found in 2-nitro-α-phenylcinnamic acid. The stability of the *trans*-form, which is common to all stilbenes, is due to the mutual repulsion of the space-filling phenyl groups. The exceptional stability of the *cis*-form in the 2-nitro-compound must indicate that there is an attraction which can overcome this normal steric effect. This may well be an association between one phenyl group and the nitro-group attached to the other, which is of the same nature as the association which gives rise to stable complexes of nitro-compounds and aromatic hydrocarbons.

Reduction of *cis*-2-nitrostilbene gives a 2-aminostilbene not known hitherto, and this is converted by boiling hydrochloric acid into an isomeride which has been obtained previously by a different method (Sachs and Hilpert, *Ber.*, 1906, **39**, 1308; Stoermer and Prigge, *loc. cit.*). Hence the first reduction product is most probably the *cis*-compound, which undergoes the normal change into the more stable *trans*-isomeride. This conclusion is supported by the decomposition of the diazo-compounds derived from the two substances. By diazotising the less stable isomeride, phenanthrene can be obtained in good yield, but none is formed from the more stable isomeride. Hence it seems likely that in the former the two phenyl groups lie on the same side of the double bond, and this simple synthesis of phenanthrene can be taken as further evidence that the less stable compound has the *cis*-configuration (V; R = Ph, R′ = H) and the isomeride previously known the *trans*-configuration (VI; R = Ph, R′ = H). It also indicates that the success of Pschorr's synthesis of phenanthrene-9-carboxylic acid from 2-amino-α-phenylcinnamic acid depends on the carboxyl group. If this is present, the stable form has the two phenyl groups on the same side of the double bond; but if it is absent, the stable form has the *trans*-configur-

ation, so the phenanthrene cannot be obtained from that form but only from the less stable isomeride.

EXPERIMENTAL.

Quinaldine.—2-Acetamidostyrene (Sabetay, Bléger, and De Lestrange, *loc. cit.*) was gently heated with 8 times its weight of phosphoryl chloride until reaction set in; after this had subsided, the mixture was boiled for 5 minutes and poured into water. From the filtered liquid, made alkaline, ether extracted quinaldine, identified by its b. p. and by the m. p. and mixed m. p. of its picrate.

Adipodi-2-vinylanilide.—1 G. of 2-aminostyrene in 10 c.c. of dry pyridine was treated with 0·8 g. of adipyl chloride drop by drop, and the mixture poured into water; the solid *product* crystallised from alcohol in colourless needles, m. p. 202° (Found: N, 8·3. $C_{22}H_{24}O_2N_2$ requires N, 8·1%).

αδ-Di-(2-quinolyl)butane (III).—The anilide was treated with phosphoryl chloride as above. The sticky solid resulting was purified by recrystallisation of its picrate from acetone in yellow needles, m. p. 224°. The picrate was decomposed with ammonia and ether, and the solid from the latter washed with light petroleum and recrystallised several times from aqueous alcohol. The *compound* formed colourless needles, m. p. 98°, soluble in all solvents except light petroleum (Found: N, 8·8. $C_{22}H_{20}N_2$ requires N, 8·9%).

2-n-*Hexamidostyrene.*—0·5 G. of 2-aminostyrene in 6 c.c. of acetone was treated with a few drops of concentrated aqueous potash and 0·6 g. of *n*-hexoyl chloride (prepared from synthetic hexoic acid; " Organic Syntheses," **4**, 11; **11**, 76) and boiled for 30 minutes. The acetone layer was poured into water; the precipitated oil solidified on standing; m. p. (from light petroleum) 61° (Found: N, 6·5. $C_{14}H_{19}ON$ requires N, 6·45%).

2-n-*Amylquinoline.*—The hexamido-compound was treated as above. A colourless basic oil was obtained, from which the picrate was prepared and crystallised repeatedly from alcohol (Found: N, 12·9. Calc.: N, 13·1%). The m. p. of the picrate was 104—105°, whereas Schopf and Lehmann (*Annalen*, 1932, **497**, 7) report 111—112°, but further recrystallisation failed to raise the m. p.

2-*Acetamidostyrene Dibromide* (IV).—0·8 G. of the styrene in chloroform was treated with 0·8 g. of bromine. The solution after concentration deposited white needles, which were recrystallised from chloroform; m. p. 125° (Found: Br, 49·75. Calc.: Br, 49·8%). A small quantity was heated with 50% alcoholic potash and diluted with water. The presence of indole was shown by colour tests with a pine shaving, with sodium nitroprusside, and with nitric and nitrous acids.

cis-2-*Nitrostilbene.*—10 G. of 2-nitro-α-phenylcinnamic acid (Pschorr, *Ber.*, 1897, **30**, 497) in 100 c.c. of quinoline were heated with 1 g. of copper chromite (Adkins and Connor, *J. Amer. Chem. Soc.*, 1931, **53**, 1092) at 200—210° until the evolution of carbon dioxide ceased (45 mins.). The mixture was then poured into 400 c.c. of 15% hydrochloric acid and extracted with ether. From the extract a brown oil was obtained, which solidified and formed yellow needles from alcohol, m. p. 62°. The compound was not transformed into an isomeride by boiling mineral acid or by exposure to sunlight in the presence of a little bromine or iodine.

cis-2-*Aminostilbene* (V; R = Ph, R′ = H).—The nitro-compound was reduced with ferrous sulphate and ammonia (Stoermer and Oehrlet, *Ber.*, 1922, **55**, 1239) or, better, by treating its solution in a mixture of equal parts of glacial acetic acid and concentrated hydrochloric acid with four times its weight of zinc dust. The amine is an oil; the m. p. of the sparingly soluble hydrochloride is 208—209°. The *acetyl* derivative, obtained with acetic anhydride, forms colourless needles (from alcohol), m. p. 112—113° (Found: N, 5·7. $C_{16}H_{15}ON$ requires N, 5·9%). When this derivative was treated with phosphoryl chloride, a brown solid of indefinite m. p. was formed. This was boiled with dilute sulphuric acid, benzaldehyde being expelled, and the solution was oxidised with acetic acid and ferric chloride; a bright red colour appeared and rosindole was slowly deposited as a red solid (cf. Freund and Le Bach, *Ber.*, 1905, **38**, 2640).

trans-2-Aminostilbene was prepared from the *cis*-compound by boiling with concentrated hydrochloric acid for 4 hours. The base obtained from the hydrochloride which separated on cooling had m. p. 101·5—102·5° (from alcohol). The acetyl derivative, m. p. 140° (cf. Sachs and Hilpert, *loc. cit.*), gave with phosphoryl chloride results similar to those obtained with the *cis*-compound.

Phenanthrene.—When *cis*-2-aminostilbene was diazotised, and the solution warmed after addition of excess of sodium carbonate, nitrogen was evolved and a brown tar separated, which solidified on cooling. Distillation under reduced pressure gave phenanthrene, recognised by

the m. p. and mixed m. p. of the substance and of its picrate. Similar treatment of the *trans*-compound gave a tar, which decomposed profoundly on attempted distillation and gave no phenanthrene.

β-4-*Bromophenylethyl Alcohol*.—16 G. of 4-aminophenylethyl alcohol (Ferber, *Ber.*, 1929, **62**, 183) were diazotised in dilute hydrobromic acid and added to a boiling cuprous bromide solution. The resulting oil was washed with alkali and distilled; b. p. 147°/10 mm. It solidified to colourless needles, m. p. 36—38°; yield, 12 g. (50%). On oxidation with permanganate, 4-bromobenzoic acid was formed. The *phenylurethane*, prepared with phenyl *iso*cyanate, formed colourless plates, m. p. 126° (from alcohol) (Found: C, 56·1; H, 4·6. $C_{15}H_{14}O_2NBr$ requires C, 56·25; H, 4·4%).

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, August 17th*, 1935.]

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37. *Studies on Hydrogen Cyanide. Part VI. The Mechanism of Gattermann's Hydrogen Cyanide Aldehyde Synthesis.*

By L. E. HINKEL, E. E. AYLING, and J. H. BEYNON.

IN the synthesis of aromatic aldehydes from phenols and phenolic ethers by means of hydrogen cyanide and hydrogen chloride in presence of aluminium chloride, Gattermann and his co-workers (*Ber.*, 1898, **31**, 1149, 1766; 1899, **32**, 278; *Annalen*, 1909, **357**, 313) considered that the primary product is iminoformyl chloride, NH:CHCl, whereas Hinkel, Ayling, and Morgan (J., 1932, 2793) regarded it as chloromethyleneformamidine, NH:CH·N:CHCl.

A valuable insight into the mechanism of the reaction is afforded by the observation (Hinkel, Ayling, and Beynon, J., 1935, 674) that the compound $AlCl_3$,2HCN unites with hydrogen chloride at 80°, forming $AlCl_3$,2HCN,HCl, identical with the product obtained by the direct union of chloromethyleneformamidine with aluminium chloride. This double compound dissociates on heating into chloromethyleneformamidine, which in presence of free aluminium chloride reacts readily with hydrocarbons and phenolic ethers, giving arylmethyleneformamidine hydrochlorides; these on hydrolysis yield the aldehydes. It is therefore not necessary to postulate the dissociation of the double compound $AlCl_3$,2HCN in the Gattermann synthesis as originally suggested (Hinkel, Ayling, and Morgan, *loc. cit.*), since it appears that hydrogen cyanide in the presence of aluminium chloride always reacts as the dimeride, giving derivatives of iminoformylcarbylamine, NH:CH·NC.

On the other hand, in the absence of aluminium chloride, a solution of hydrogen chloride in hydrogen cyanide consists potentially of iminoformyl chloride, although distillation leads to the recovery of the hydrogen cyanide, and the only compound isolated is the sesquichloride, dichloromethylformamidine hydrochloride (compare Hinkel and Dunn, J., 1930, 1836). Therefore, when hydrogen cyanide and hydrogen chloride react with resorcinol in ethereal solution (Gattermann and Köbner, *Ber.*, 1899, **32**, 278) or with ethyl alcohol (Pinner, *Ber.*, 1883, **16**, 352), the resulting hydrochloride of resorcylaldimine or of iminoformyl ethyl ether, respectively, must owe its formation to the presence of iminoformyl chloride. These reactions definitely confirm the primary reaction as the tendency to form iminoformyl chloride before derivatives of the dimeride, iminoformylcarbylamine, since the latter, when treated in a similar manner, yields formamidine hydrochloride and ethyl orthoformate (Hinkel, Ayling, and Beynon, *loc. cit.*).

When hydrogen cyanide is replaced by iminoformylcarbylamine in the resorcylaldehyde synthesis, a somewhat similar reaction occurs. In place of the white or pink-tinged resorcylaldimine hydrochloride, however, yellow *resorcylmethyleneformamidine hydrochloride*, $C_6H_3(OH)_2$·CH:N·CH:NH,HCl, separates, and this, on hydrolysis, also yields resorcylaldehyde. The primary reaction in this case is the formation of chloromethyleneformamidine, which then reacts directly with resorcinol. The yellow compound so formed is not decomposed into the aldimine hydrochloride by excess of hydrogen chloride or resorcinol.

In the similar action with hydrogen cyanide, the presence of the formamidine derivative has not been detected and no derivative of iminoformylcarbylamine results unless the temperature is kept at 0° throughout. Under the latter condition, the reaction between the iminoformyl chloride and resorcinol is depressed so that part of the hydrogen cyanide appears as the "sesquichloride," admixed with the resorcylaldimine hydrochloride.

The exact mode of formation of the sesquichloride from hydrogen cyanide and hydrogen chloride is still not clear, but the initial stage must be the formation of iminoformyl chloride, which only exists potentially, similarly to formyl chloride. In the absence of any reactive substance, such as resorcinol or alcohol, the molecules of iminoformyl chloride combine to form chloromethyleneformamidine: NH:CHCl + NH:CHCl ⟶ NH:CH·N:CHCl. Since, however, the latter does not yield the sesqnichloride with hydrogen chloride (Hinkel and Dunn, *loc. cit.*), it is probable that, only during the moment of union of the molecules of iminoformyl chloride, at the low temperature, can the further combination with hydrogen chloride occur.

EXPERIMENTAL.

Action of Hydrogen Cyanide and Hydrogen Chloride upon Resorcinol in Ether.—(i) *At room temperature.* When an experiment was carried out under the conditions used by Gattermann and Köbner (*Ber.*, 1899, **32**, 278), the yield of resorcylaldehyde (calculated on the resorcinol taken) was 58%, in close agreement with that obtained by Hinkel, Ayling, and Morgan (J., 1932, 2793). Dilution of the decanted ether with an equal volume of dry ether caused a further precipitation of the aldimine hydrochloride, m. p. 166° (decomp.), thereby giving a total yield of resorcylaldehyde of 72%.

(ii) *At* 0°. When the above experiment was repeated at 0°, the crystalline solid obtained, m. p. 166—170° (decomp.) (Found: N, 10·0; Cl, 31·7%), corresponded to a mixture of the aldimine hydrochloride (Calc.: N, 8·1; Cl, 20·5%) and the sesquichloride (Calc.: N, 17·1; Cl, 65·1%). Hydrolysis of the solid yielded resorcylaldehyde (56%, calculated on the resorcinol used).

An almost complete conversion of the resorcinol into the aldehyde can be obtained only when the hydrogen cyanide is in excess and the experiment is carried out at laboratory temperature, and even then the aldimine hydrochloride first precipitated is always contaminated with some sesquichloride.

Other solvents, such as tetrachloroethane, *o*-dichlorobenzene, chlorobenzene, and benzene, can replace the ether in the preparation.

Action of Iminoformylcarbylamine and Hydrogen Chloride upon Resorcinol.—When dry hydrogen chloride was slowly passed into a solution of iminoformylcarbylamine (Hinkel, Ayling, and Beynon, *loc. cit.*) (1 g.; 1 mol.) and resorcinol (2·6 g.; 1·2 mols.) in dry ether (100 c.c.) under a reflux condenser at room temperature with exclusion of moisture, a bright yellow powder began to be deposited after 15 minutes. It was collected after 3 hours, washed with ether (40 c.c.), and dried in a vacuum, yielding *resorcylmethyleneformamidine hydrochloride*, m. p. 135° (decomp.) (Fonnd: N, 14·0; Cl, 17·8. $C_8H_9O_2N_2Cl$ requires N, 14·0; Cl, 17·7%). Yield, 3·6 g. (97%, calculated on the iminoformylcarbylamine). The yellow compound (2·5 g.), when boiled for 5 minutes with water (10 c.c.) and 4*N*-hydrochloric acid (1 c.c.), yielded resorcylaldehyde (1·6 g.; 93%) as golden-yellow needles, m. p. and mixed m. p. 135°.

Action of Chloromethyleneformamidine upon Resorcinol.—Resorcinol (2·4 g.; 1 mol.) was shaken for 12 hours with a suspension of finely powdered chloromethyleneformamidine (Hinkel, Ayling, and Beynon, *loc. cit.*) (2 g.; 1 mol.) in dry ether (20 c.c.) in a sealed flask at room temperature. The yellow powder obtained, after being washed with ether (20 c.c.) and dried in a vacuum, yielded resorcylmethyleneformamidine hydrochloride (4 g.; 90%), m. p. 135° (decomp.). Hydrolysis of the compound (2 g.) with dilute acid as above yielded resorcylaldehyde (1·2 g.; 87%).

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UNIVERSITY COLLEGE, SWANSEA. [*Received, October 22nd*, 1935.]

38. *The Simultaneous Formation of Two Isomeric* iso*Propylidene Derivatives of 2-Methyl γ-Methylglucoside.*

By D. J. Bell.

RECENT experiments in this laboratory demanded that the position of the hydroxyl groups involved in the condensation with acetone of 2-methyl γ-methylglucoside should be determined. Macdonald (J., 1913, **103**, 1896) and Irvine, Fyffe, and Hogg (J., 1915, **107**, 524) concluded from the evidence then available that *iso*propylidene γ-methylglucoside had free hydroxyls in positions 2 and 3. The discovery of *iso*diacetoneglucose (1 : 2 : 3 : 5) by Freudenberg *et al.* (*Ber.*, 1928, **61**, 1735) and of 3 : 5-benzylidene *iso*propylidene glucose by Brigl and Grüner (*Ber.*, 1932, **65**, 1428), coupled with the spatial position in glucofuranose of hydroxyl groups 3 and 5, rendered not impossible a configuration alternative to that suggested by the original workers in this field. As detailed below, the present author finds that condensation between acetone and 2-methyl γ-methylglucoside, catalysed by 1% sulphuric acid and anhydrous copper sulphate, leads to the formation of a mixture of 3 : 5- and 5 : 6-iso*propylidene* derivatives.

The steps in the investigation may be summarised as follows: (1) Condensation of acetone with the glucoside, (2) methylation of vacant hydroxyl groups, (3) hydrolysis of glucosidic methyl and *iso*propylidene groups, (4) conversion of free sugars into β-glucosides, (5) isolation of crystalline 2 : 3-dimethyl β-methylglucoside 4 : 6-dinitrate, (6) isolation of crystalline 3 : 4-di-*p*-toluenesulphonyl 2 : 6-dimethyl β-methylglucoside. No attempt was made to conduct a quantitative examination of the relative amounts of the two *iso*propylidene isomerides.

EXPERIMENTAL.

Condensation of Acetone and 2-Methyl γ-Methylglucoside.—To 13 g. of the glucoside (Oldham and Rutherford, *J. Amer. Chem. Soc.*, 1932, **54**, 1086), dissolved in 150 ml. of acetone, 25 g. of anhydrous copper sulphate and 1·5 ml. of concentrated sulphuric acid were added and the whole was kept at room temperature for 18 hours. After filtration to remove inorganic material, the acetone was distilled off under reduced pressure, in the presence of a little sodium carbonate. The residue was dissolved in water, filtered through norit, and extracted six times with chloroform. The extract, after dehydration, was evaporated to dryness in a vacuum, 11·5 g. of a colourless, fairly mobile syrup being obtained (Found: OMe, 25·4. $C_{11}H_{20}O_6$ requires OMe, 25·4%).

Methylation of the product. 11 G. were twice methylated with Purdie's reagents, a very mobile, colourless syrup (11 g.) having the composition of a trimethyl *iso*propylidene hexose being obtained (Found: OMe, 35·4. $C_{12}H_{22}O_6$ requires OMe, 35·5%).

Aqueous-acid hydrolysis. 10 G. of the above product were hydrolysed by heating at 100° in 100 ml. of 0·5% hydrochloric acid until constant polarimetric readings were obtained (180 mins.). After neutralisation with silver carbonate and extraction of the crude product with ethyl acetate, 7·0 g. (84%) of dimethylated sugars were obtained as a colourless glass.

Conversion into β-glucosides. This was effected by the procedure of Oldham (*J. Amer. Chem. Soc.*, 1934, **56**, 1360). The crude yield was 4·0 g., but after 4 hours' boiling with *N*/70-hydrochloric acid to eliminate furanosides, the yield fell to 3·25 g.

Isolation of 2 : 3-*Dimethyl β-Methylglucoside* 4 : 6-*Dinitrate.*—2 G. of the crude dimethyl methylglucoside were converted into the dinitric ester as described by Oldham and Rutherford (*J. Amer. Chem. Soc.*, 1932, **54**, 366). The product was a mixture of syrup and crystals (yield, 0·7 g.), m. p. 99—100°, $[\alpha]_D^{20^\circ}$ − 20·8° (in chloroform; $l = 2$, $c = 4·0$). Oldham and Rutherford record for 2 : 3-dimethyl β-methylglucoside 4 : 6-dinitrate, m. p. 98—99° and $[\alpha]_D$ − 20·8°. The m. p. of a mixture of a specimen of this substance with the product described above showed no depression (Found: OMe, 29·9. Calc. for $C_9H_{16}O_{10}N_2$: OMe, 29·9%).

Isolation of 3 : 4-*Di*-p-*toluenesulphonyl* 2 : 6-*Dimethyl β-Methylglucoside.*—The syrupy portion (1·7 g.) of the crude dinitrate was denitrated with zinc and iron in acetic acid. After appropriate isolation, the resulting glucoside (1·0 g.) showed $[\alpha]_D^{20^\circ}$ − 22° (in chloroform) (2 : 3-dimethyl β-methylglucoside has $[\alpha]_D$ − 45°; Oldham, *loc. cit.*). It was converted into the ditoluenesulphonate in the usual way, a crystalline product being obtained; the m. p., however, indicated that it was a mixture. 1·91 G. were treated by the processes described by Oldham

and Rutherford (*J. Amer. Chem. Soc.*, 1932, **54**, 366) by which a nitro-group is substituted for a toluenesulphonyl group in position 6; any 2 : 3-dimethyl derivative present was thus rendered more soluble. On treatment of the crude product with ether, crystals separated. These, on recrystallisation from alcohol containing 10% of acetone, yielded 0·5 g. of needles, m. p. 157—159°, $[\alpha]_D^{20°}$ − 8·9° (in chloroform; l = 2, c = 3·0). A mixed m. p. determination with 3 : 4-ditoluenesulphonyl 2 : 6-dimethyl β-methylglucoside ($[\alpha]_D$ − 8·8°; Oldham and Rutherford) showed no depression (Found : OMe, 17·4. Calc. for $C_{23}H_{30}O_{10}S_2$: OMe, 17·5%).

The author is indebted to the Commissioners for the Exhibition of 1851 for the award of a Senior Studentship and to the Medical Research Council for a grant.

MARISCHAL COLLEGE, UNIVERSITY OF ABERDEEN. [*Received, November 30th*, 1935.]

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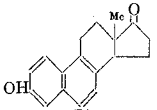
39. *Syntheses of Polycyclic Compounds related to the Sterols. Part V. Methoxy- and Hydroxy-derivatives of Phenanthrene.*

By G. A. R. KON and F. C. J. RUZICKA.

THE appearance of a recent paper by Butenandt and Schramm (*Ber.*, 1935, **68**, 2083) makes it desirable to place on record some experiments on the preparation of methoxylated derivatives of naphthalene and phenanthrene, which were to be employed in the synthesis of compounds related to equilenin (I). Other objects of the work were the preparation of compounds which might from their constitution be expected to show oestrogenic properties, and the study of the effect of changes of structure on the latter.

Cook, Dodds, and Hewett have stated (*Nature*, 1933, **131**, 205) that 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (II) is oestrogenic (see, however, Butenandt, *loc. cit.*) and it



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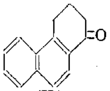

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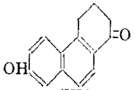
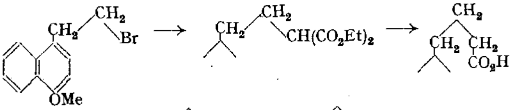


(III.)

appeared to be of interest to examine the effect of introducing into different positions in the molecule of this compound the phenolic group characteristic of both equilenin and oestrone. The preparation of the 7-hydroxy-compound (III) has since been carried out by Butenandt (*loc. cit.*); that of the 8- and the 9-isomeride is now described. Both these compounds were obtained by the same method, starting from the appropriate methoxy-naphthylethyl alcohols, the preparation of which had been undertaken with a view to the first object of the present work. The alcohol was converted into the bromide, which was condensed with ethyl sodio- or potassio-malonate; the ester was hydrolysed, the acid decarboxylated, and the new acid cyclised :



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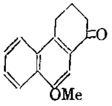
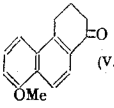


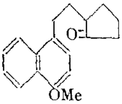


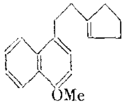
(V.)

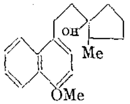
Finally, the methoxy-ketone was converted into the free phenol.

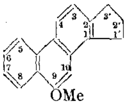
The preparation of the 9-methoxy-compound (IV) proceeded smoothly, but when aluminium chloride was used for the final stage in the preparation of the 8-methoxy-compound, an abnormal *product*, m. p. 88—89°, was formed; it had the expected composition, but did not react with semicarbazide and gave on demethylation a *substance* of the formula $C_{14}H_{14}O_3$, not $C_{14}H_{12}O_2$. The *isomeride*, m. p. 137°, formed when stannic chloride was used in place of aluminium chloride reacted with semicarbazide and behaved normally on demethylation, yielding a *phenol* which was reconverted into the methoxy-compound, m. p. 137°, on methylation; this is therefore regarded as having the structure (V)—that of its isomeride has not yet been elucidated.

β-4-*Methoxy*-1-*naphthylethyl alcohol* was obtained by treating the Grignard reagent prepared from 1-bromo-4-methoxynaphthalene with ethylene oxide. The corresponding *bromide* was condensed with ethyl *cyclo*pentanone-2-carboxylate, and the resulting *ester* hydrolysed to α-(β'-4-*methoxy*-1-*naphthylethyl*)*adipic acid*; on pyrolysis, this acid did not give the expected substituted *cyclo*pentanone (VI), but underwent fission to 4-*methoxy*-1-*methylnaphthalene*. The corresponding alcohol should have resulted from the action of the Grignard reagent of the above bromide on *cyclo*pentene oxide (compare Fulton and Robinson, J., 1933, 1463), but under the conditions of the experiment the greater part was dehydrated to 4-*methoxy*-1-β-cyclo*pentenylethylnaphthalene* (VII). This was cyclised to the tetracyclic *compound* by phosphoric oxide, as shown by the formation of *cyclo*pentenophenanthrene on dehydrogenation with selenium at 320—350°, the methoxyl group being eliminated under these somewhat drastic conditions. A better result was obtained by treating the same Grignard reagent with 2-methyl*cyclo*pentanone; the *carbinol* (VIII) cyclised readily and the *methoxy-hydrocarbon* gave on dehydrogenation under carefully controlled conditions 9-*methoxy*-1 : 2-cyclo*pentenophenanthrene* (IX); the preparation of this compound was of importance because the position of the methoxyl group in the dehydrogenation product of oestrone methyl ether (Cook and Girard, *Nature*, 1934, **133**, 377) was not known at the time; the two compounds have quite different properties.


(VI.)


(VII.)


(VIII.)


(IX.)

9-*Methoxy*-3'-*methyl*-1 : 2-cyclo*pentenophenanthrene*, which was required for crystallc graphic work, was similarly prepared from 2 : 5-dimethyl*cyclo*pentanone.

β-5-*Methoxy*-1-*naphthylethyl alcohol* was prepared in the same way as the 4 : 1-compounc starting from 1-bromo-5-methoxynaphthalene (Fuson, *J. Amer. Chem. Soc.*, 1924, **4** 2785), the preparation of which has been modified. 8-*Methoxy*-1 : 2-cyclo*pentenophena* *threne* was synthesised from this by a method similar to that described above and was al found to differ appreciably from the isomeride derived from equilenin; these compound unlike *cyclo*pentenophenanthrene and its 3'-methyl derivative, depress each other's m. and their identification is therefore more certain.

The results of the biological tests now being carried out on some of the compounc described will be reported elsewhere.

EXPERIMENTAL.

β-4-*Methoxy*-1-*naphthylethyl Alcohol*.—To an ice-cold Grignard reagent, prepared at roo temperature from 124 g. of 1-bromo-4-methoxynaphthalene (Fourneau, Tréfouel, and Tréfou *Bull. Soc. chim.*, 1928, **43**, 454) and 12·9 g. of magnesium activated with iodine in 500 c.c. ether, were added 28 g. of ethylene oxide in 250 c.c. of ether. The mixture was mechanical stirred during the addition, then allowed to attain room temperature, and finally warmed und reflux, and the ether distilled off. The mass was decomposed with ice and hydrochloric aci and the products taken up in ether, dried, and distilled. There was a considerable low fractio b. p. 110—150°/2 mm. (mainly α-naphthyl methyl ether), then the *alcohol* distilled at 190°/2 mi

(60 g.) and solidified; m. p. 87° after repeated crystallisation from benzene-petroleum (Found: C, 76·8; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·1; H, 7·0%).

Bromide. Heating with 33% hydrogen bromide in acetic acid under pressure, or with hydrobromic acid and sulphuric acid, failed to convert the alcohol satisfactorily into the bromide, the product generally containing unchanged alcohol. Finally, 20 g. of the alcohol in 120 c.c. of benzene were vigorously stirred during the slow addition of 25 g. of phosphorus tribromide in 70 c.c. of benzene, the mixture being then warmed under reflux for 2 hours; 17 g. of the *bromide* were obtained as a yellow oil, b. p. 161°/1·2 mm. (Found: Br, 30·2. $C_{13}H_{13}OBr$ requires Br, 30·2%).

Ethyl 2-(β-4-*Methoxy*-1-*naphthylethyl*)cyclo*pentanone*-2-*carboxylate*.—4·7 G. of "molecular" potassium were treated with 18 g. of ethyl *cyclo*pentanone-2-carboxylate in 70 c.c. of dry xylene, warming on the steam-bath for 45 minutes completing the reaction; 17 g. of the above bromide were then added and the mixture was boiled under reflux (oil-bath) for 48 hours. The *ester*, isolated in the usual manner, was a very viscous, yellow oil, b. p. 235—248°/1·2 mm. (Found: C, 73·6; H, 7·3. $C_{21}H_{24}O_4$ requires C, 74·0; H, 7·3%).

α-(β′-4-*Methoxy*-1-*naphthylethyl*)*adipic Acid*.—The above ester was boiled with twice its weight of potassium hydroxide in 40% aqueous solution, together with enough alcohol to give a homogeneous solution, for 16 hours, the alcohol being allowed to distil off slowly. The *acid* was isolated by acidification and extraction with ether and slowly solidified on keeping and scratching; m. p. 178° after crystallisation from alcohol (Found: C, 68·7; H, 6·6. $C_{19}H_{22}O_5$ requires C, 69·0; H, 6·7%).

Pyrolysis. The crude acid was heated with a trace of baryta under 450 mm. by means of an air-bath; a liquid distilled at 200—240°. In another experiment at atmospheric pressure, the product boiled at 330—360°, 121°/0·8 mm. on redistillation (21 g. from 50 g. of ketonic ester) and consisted of 4-*methoxy*-1-*methylnaphthalene* (Found: C, 83·7; H, 7·1. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%). The same substance was synthesised by the action of methyl iodide on the Grignard reagent prepared from 1-bromo-4-methoxynaphthalene; it can be characterised by means of the picrate, m. p. 146—147°, the *s*-trinitrobenzene complex, m. p. 169°, and the trinitrotoluene complex, m. p. 75—76°.

β-4′-*Methoxy*-1′-*naphthylethyl*cyclo*pentene*.—12 G. of *cyclo*pentene oxide in ether were gradually added with constant stirring to an ice-cold Grignard reagent prepared from 25 g. of β-4-methoxy-1-naphthylethyl bromide exactly as described on p. 188; the mixture was then warmed under reflux for an hour. On distillation of the ether a sudden vigorous reaction took place and the contents of the flask swelled and became solid. The products were isolated in the usual way and the portion boiling above 190°/1 mm. was redistilled; 6 g., boiling at 150—160°/0·02 mm., consisted largely of the unsaturated *methoxy-hydrocarbon* (VII), though it doubtless contained some of the carbinol originally formed (Found: C, 84·1, 83·8; H, 7·9, 7·8. $C_{18}H_{20}O$ requires C, 85·6; H, 8·0%. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%). The methoxy-hydrocarbon formed a *s*-trinitrobenzene *complex*, orange needles, m. p. 107—108° (Found: C, 61·8; H, 4·9. $C_{24}H_{23}O_7N_3$ requires C, 61·9; H, 5·0%). There was also a fraction, b. p. 220—240°/0·02 mm., which doubtless consisted of αδ-*di*-(4-*methoxy*-1-*naphthyl*)*butane*, prisms, m. p. 124°, from alcohol-benzene (Found: C, 84·3; H, 7·0. $C_{26}H_{26}O_2$ requires C, 84·3; H, 7·1%); it was characterised by a picrate, red needles, m. p. 173°, a *s*-trinitrobenzene complex, orange-red needles, m. p. 189—190°, and a trinitrotoluene complex, yellow needles, m. p. 140°. The fraction of lowest b. p., 97—140°/1 mm., probably contained 4-methoxy-1-ethylnaphthalene, forming a reddish picrate, m. p. 126°, and an orange *s*-trinitrobenzene complex, m. p. 162°.

9-*Methoxy*-3 : 4-*dihydro*-1 : 2-cyclo*pentanophenanthrene*.—5 G. of the crude methoxy-hydrocarbon described above were heated with 10 g. of phosphoric oxide at 130—140° for 30 minutes, and the product isolated by addition of ice and ether. The yellow oil obtained had b. p. 185—186°/0·8 mm. (Found: C, 85·3; H, 7·9. $C_{18}H_{20}O$ requires C, 85·6; H, 8·0%) and formed a *s*-trinitrobenzene *complex*, orange needles, m. p. 166° (Found: C, 61·9; H, 5·0. $C_{24}H_{23}O_7N_3$ requires C, 61·9; H, 5·0%). On dehydrogenation with selenium at 340—345° a small amount of *cyclo*pentenophenanthrene was formed.

2-*Methyl*-1-β-4′-*methoxy*-1′-*naphthylethyl*cyclo*pentanol* (VIII).—29 G. of 2-methyl*cyclo*pentanone in 50 c.c. of ether were slowly added to a well-stirred, ice-cold Grignard reagent prepared from 59 g. of β-4-methoxy-1-naphthylethyl bromide, and the mixture warmed under reflux for 3 hours. On working up as before, 19 g. of a fraction, b. p. 185—190°/0·1 mm., were obtained, consisting of the desired *carbinol* (Found: C, 80·0; H, 8·4. $C_{19}H_{24}O_2$ requires C, 80·2; H, 8·3%). There was also a low fraction, b. p. 141—145°/0·1 mm. after redistillation (Found: C, 78·8, 79·1; H, 9·1, 8·8%), forming a red picrate, m. p. 112—113°, and a *s*-trinitro-

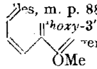
benzene complex, m. p. 129—130°, which was not further investigated. The high fraction consisted of the dinaphthylbutane derivative already described.

9-*Methoxy*-1-*methyl*-3 : 4-*dihydro*-1 : 2-cyclo*pentanophenanthrene*.—The cyclisation of the carbinol, carried out as described above, gave the *methoxy-hydrocarbon* in good yield, as a very viscous, yellow oil, b. p. 165—170°/0·1 mm. after distillation over sodium (Found : C, 85·4; H, 8·4. $C_{19}H_{22}O$ requires C, 85·6; H, 8·3%); the picrate formed red needles, m. p. 138°, and the *s*-trinitrobenzene complex, orange needles, m. p. 149°.

Dehydrogenation. 10 G. of the methoxy-hydrocarbon were heated with 8·7 g. of selenium powder for 20 hours to 340—345° (bath temperature); some 2 g. of dehydrogenation product were obtained and identified as 1 : 2-*cyclo*pentenophenanthrene by analysis (Found : C, 93·2; H, 6·6. Calc. : C, 93·5; H, 6·5%) and by the preparation of derivatives. Another attempt under similar conditions gave material containing some oxygen. When the experiment was repeated, 12 g. of selenium being used and the bath temperature kept at 280—290° for 21 hours, 5 g. of almost colourless solid were obtained after distillation in a high vacuum, consisting of the desired 9-*methoxy*-1 : 2-cyclo*pentenophenanthrene* (IX), crystallising in plates from petroleum and in needles from alcohol, m. p. 129° (Found : C, 86·8; H, 6·6. $C_{18}H_{16}O$ requires C, 87·1; H, 6·4%). The *picrate* formed reddish needles, m. p. 124° (Found : C, 60·4, 60·1, 60·4; H, 5·1, 4·7, 4·9.* $C_{24}H_{19}O_8N_3$ requires C, 60·4; H, 4·0%); the *s*-trinitrobenzene *complex*, orange needles, m. p. 132° (Found : C, 62·4, 62·3; H, 5·0, 4·8. $C_{24}H_{19}O_7N_3$ requires C, 62·5; H, 4·1%), the trinitrotoluene *complex*, deep yellow needles, m. p. 105—106° (Found : C, 62·9, 63·2, 63·4; H, 5·3, 5·5, 5·4. $C_{25}H_{21}O_7N_3$ requires C, 63·1; H, 4·5%), and the styphnate, yellow needles, m. p. 122°. The m. p.'s of all these derivatives were considerably depressed on admixture of the relevant derivatives of *cyclo*pentenophenanthrene.

2 : 5-*Dimethyl*-1-β-4′-*methoxy*-1′-*naphthylethyl*cyclo*pentanol* was obtained in the same way as the lower homologue, 2 : 5-dimethyl*cyclo*pentanone being used; the yield was even better; b. p. 195—200°/0·2 mm. (Found : C, 80·8; H, 8·7. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·7%).

9-*Methoxy*-1 : 3′-*dimethyl*-3 : 4-*dihydro*-1 : 2-cyclo*pentanophenanthrene*.—On dehydration of the above alcohol a good yield of the *methoxy-hydrocarbon* was obtained as a yellow oil, b. p. 180—183°/0·3 mm. (Found : C, 85·4; H, 8·7. $C_{20}H_{24}O$ requires C, 85·6; H, 8·6%), giving a *picrate*, red needles, m. p. 119—120° (Found : C, 61·1; H, 5·3. $C_{26}H_{27}O_8N_3$ requires C, 61·3; H, 5·3%), a *s*-trinitrobenzene *complex*, dark orange needles, m. p. 140—141° (Found : 63·0; H, 5·5. $C_{26}H_{27}O_7N_3$ requires C, 63·3; H, 5·5%), and a trinitrotoluene complex, yellow ...es, m. p. 88°.



...*hoxy-3′-methyl*-1 : 2-cyclo*pentenophenanthrene*.—When 13·5 g. of the above compound ...enated at 280—290°, 11 g. of product, b. p. 185—190°/0·4 mm., were obtained; ... chromatographic adsorption (compare Gamble, Kon, and Saunders, J., ...tallised from alcohol, forming needles, m. p. 111° (Found : C, 87·0; ... H, 6·9%). The *picrate* formed long red needles, m. p. 147° ...quires C, 61·1; H, 4·3%), the *s*-trinitrobenzene complex, ...trotoluene complex, light orange needles, m. p. 104°.

OMe

(VI.)

9-*Methoxy-3′-methyl*-1 : 2-cyclo...
graphic work, was similarly prepared f...
β-5-*Methoxy*-1-*naphthylethyl alcohol* was ...e preparation of 1-bromo-5-methoxynaphthalene
starting from 1-bromo-5-methoxynaphthalen... duce 1-bromo-5-nitronaphthalene by West's
2785), the preparation of which has been mod... resulting amine into the bromonaphthol was
threne was synthesised from this by a method si... etic acid and adding 1130 c.c. of sulphuric
found to differ appreciably from the isomeride ... stirring. The resulting fine suspension of
unlike *cyclo*pentenophenanthrene and its 3′-me... dium nitrite in 870 c.c. of water, 30·5 g. of
and their identification is therefore more certai... ling solution of 1120 c.c. of sulphuric acid in
The results of the biological tests now be... 5 g. of almost pure bromonaphthol separated
described will be reported elsewhere. ... ol. The preparation of the *alcohol* was carried
... were not so good (13 g. from 50 g. of bromide);
EXPER... d and then crystallised from petroleum (b. p.
... C, 76·7; H, 7·2. $C_{13}H_{14}O_2$ requires C, 77·1;
β-4-*Methoxy*-1-*naphthylethyl Alcohol*.—To ... of ethylene oxide was used in the preparation;
temperature from 124 g. of 1-bromo-4-meth... re crystallised from benzene–petroleum in needles,
Bull. Soc. chim., 1928, **43**, 454) and 12·9 g... osition $C_{13}H_{10}O_5$ (Found : C, 59·5; H, 4·1. Calc. :
ether, were added 28 g. of ethylene oxide... stigated.
stirred during the addition, then allowed
reflux, and the ether distilled off. The give unaccountably high values for hydrogen; they were
and the products taken up in ether, dri... ford and Dr. A. Schoeller of Berlin, whose results show a
b. p. 110—150°/2 mm. (mainly α-naph...

The *bromide*, prepared from the alcohol by means of phosphorus tribromide, had b. p. 180°/1·7 mm. (Found : Br, 29·9. $C_{13}H_{13}OBr$ requires Br, 30·1%); the yield from 38 g. of the alcohol was 32 g.

2-*Methyl*-1-(β-5′-*methoxy*-1′-*naphthylethyl*)cyclo*pentanol*.—This compound was prepared from the above bromide in exactly the same way as its isomeride (VIII) and the fraction, b. p. 190°—195°/0·1 mm., was comparable in yield with the corresponding fraction (Found : C, 80·8; H, 8·6. $C_{19}H_{24}O_2$ requires C, 80·3; H, 8·5%). The analysis figures suggest that the alcohol had undergone dehydration to a small extent; it gave a *s*-trinitrobenzene complex, m. p. 110—111°. The high fraction, b. p. 240—250°/0·1 mm., consisted of αδ-*di*-(5-*methoxy*-1-*naphthyl*)-*butane*, forming prisms, m. p. 176°, from benzene–alcohol (Found : C, 84·1; H, 7·2. $C_{26}H_{26}O_2$ requires C, 84·3; H, 7·1%); the picrate had m. p. 205°, the *s*-trinitrobenzene complex, m. p. 228°, and the trinitrotoluene complex, m. p. 146°.

8-*Methoxy*-1-*methyl*-3 : 4-*dihydro*-1 : 2-cyclo*pentanophenanthrene*.—The dehydration of 22 g. of the carbinol as described on p. 189 gave 16 g. of the *methoxy-hydrocarbon*, b. p. 185°/0·3 mm. (Found : C, 85·3; H, 8·4. $C_{19}H_{22}O$ requires C, 85·6; H, 8·3%). This formed a picrate, red needles, m. p. 158°, and a *s*-trinitrobenzene complex, orange needles, m. p. 135°.

8-*Methoxy*-1 : 2-cyclo*pentenophenanthrene*.—The dehydrogenation of the above compound at 290° for 19 hours gave a good yield of product, which was purified twice by chromatographic adsorption and finally recrystallised from alcohol, forming long needles, m. p. 153° (Found : C, 86·9; H, 6·7. $C_{18}H_{16}O$ requires C, 87·1; H, 6·4%). The *picrate* formed reddish needles, m. p. 160° (Found : C, 60·3; H, 4·3. $C_{24}H_{19}O_8N_3$ requires C, 60·4; H, 4·0%), and the *s*-trinitrobenzene *complex*, light orange needles, m. p. 194° (Found : C, 62·4; H, 4·2. $C_{24}H_{19}O_7N_3$ requires C, 62·5; H, 4·1%).

β-5-*Methoxy*-1-*naphthylethylmalonic Acid*.—70 G. of ethyl malonate were gradually added to 7·1 g. of "molecular" potassium, suspended in xylene, and the reaction was completed by warming for an hour; 55 g. of β-5-methoxy-1-naphthylethyl bromide were then added and the mixture was heated in an oil-bath at 150° for 45 hours. The product was isolated by means of ether, freed from solvents, and distilled, 35 g. being collected between 205° and 210°/0·8 mm. A considerable lower-boiling fraction was also collected, which solidified and formed plates from methyl alcohol, m. p. 70—71°, apparently of the composition $C_{13}H_{12}O_7$ (Found : C, 55·8; H, 4·4. Calc. : C, 55·7; H, 4·3%); it has not been further investigated.

The ester was directly hydrolysed to the *acid* by warming it over-night with an excess of 30% aqueous sodium hydroxide and enough alcohol to give a homogeneous solution; a crystalline, sparingly soluble sodium salt soon began to separate. On acidification a theoretical yield of the acid was precipitated; this formed plates, m. p. 182° (decomp.), from ethyl acetate–petroleum (Found : C, 66·6; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6%).

γ-5-*Methoxy*-1-*naphthylbutyric Acid*.—The malonic acid (28 g.) was heated under reduced pressure above its m. p., the melt dissolved in 1 l. of 5% aqueous sodium hydroxide, and the solution extracted with ether and acidified. The *acid* was recrystallised from dilute alcohol (charcoal) and finally from ethyl acetate–petroleum (b. p. 80—100°), 17 g. of pure product, m. p. 143°, being obtained (Found : C, 73·7; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·6%).

Cyclisation. (i) 5 G. of the acid were boiled for ¾ hour with 25 c.c. of chloroform and 6 c.c. of thionyl chloride, the solvent removed under reduced pressure, and the residue twice evaporated under reduced pressure with benzene to ensure the complete removal of the thionyl chloride. 25 C.c. of tetrachloroethane were added and 6 g. of finely powdered aluminium chloride were introduced in three portions into the ice-cold solution, which was then kept in ice for a further 16 honrs. The product was worked up in the usual way, taken up in ether, freed from solvent, and distilled, a brown oil (1·9 g.) being obtained. When rubbed with methyl alcohol, this solidified; it then crystallised from dilute methyl alcohol (charcoal) in plates, m. p. 88—89° (Found : C, 79·4; H, 6·5. $C_{15}H_{14}O_2$ reqnires C, 79·6; H, 6·2%). This material did not form a semicarbazone, although the mother-liquors from its preparation gave a small amount of sparingly soluble precipitate, m. p. 224°, on treatment with semicarbazide acetate.

The compound was converted into the free phenol by boiling 0·8 g. with 36 c.c. of acetic acid and 45 c.c. of hydrobromic acid (*d* 1·45) for 3 hours. The acetic acid was distilled off under reduced pressure, the solid product purified by reprecipitation from an alkaline solution and finally isolated by means of ether as a dark solid mass; this was sublimed at 135°/0·02 mm., giving a cream-coloured solid, which crystallised from chloroform–petroleum in small needles, m. p. 155°, and gave a bluish-violet colour with alcoholic ferric chloride; its composition appeared to be $C_{14}H_{14}O_3$ and it did not give the original methoxy-compound on methylation with methyl sulphate in alkaline solution (Found : C, 73·2; H, 6·6. Calc. : C, 73·1; H, 6·2%).

(ii) The acid was cyclised with stannic chloride exactly as described by Haworth and Sheldrick (J., **1934**, 867), and the product isolated in the same way. Some acid was recovered, and a 40% yield of neutral solid obtained. This was recrystallised from methyl alcohol with a little water, forming small needles, m. p. 137°, evidently consisting of 1-*keto*-8-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (V) (Found : C, 79·7; H, 6·4. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%); it formed a very sparingly soluble semicarbazone, m. p. 272°. The methoxy-ketone was demethylated as described above, the *hydroxy-ketone* being finally sublimed at 0·02 mm.; it formed small yellowish needles, m. p. 256°, from acetone–petroleum (b. p. 60—80°), and was reconverted into the methoxy-ketone, m. p. 137°, on methylation (Found : C, 79·4; H, 5·8. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·7%).

β-4-*Methoxy*-1-*naphthylethylmalonic Acid* [with C. Simons].—23 G. of β-4-methoxy-1-naphthylethyl bromide were warmed over-night with 27 g. of ethyl malonate and 2·2 g. of sodium in 40 c.c. of absolute alcohol; 21 g. of the new ester, b. p. 210°/3—5 mm., were isolated, and hydrolysed as described on p. 191, giving 18 g. of the *acid*, which was recrystallised from dilute alcohol and then from ethyl acetate–petroleum, forming stout prisms, m. p. 180° (decomp.) (Found : C, 66·5; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6%).

γ-4-*Methoxy*-1-*naphthylbutyric Acid*.—The decarboxylation of the malonic acid and the purification of the product were carried out as described on p. 191 and the *acid* was crystallised from dilute alcohol; m. p. 131° (Found : C, 73·9; H, 6·7. $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·6%).

1-*Keto*-9-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IV).—The cyclisation of the acid (12 g.) was carried out with aluminium chloride and gave 9·5 g. of oil, b. p. 224°/1·2 mm.; this slowly solidified and formed fine prisms, m. p. 98°, from dilute methyl alcohol (Found : C, 79·7; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·2%).

1-*Keto*-9-*hydroxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—The methoxy-ketone was demethylated as described on p. 191, giving a good yield of the *phenol*, which was purified by vacuum sublimation and recrystallisation from benzene–petroleum and formed small crystals, m. p. 260° (Found : C, 79·3; H, 5·6. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·7%); it gave a faint white precipitate with alcoholic ferric chloride.

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Imperial College, London, S.W. 7. [*Received, December 7th*, 1935.]

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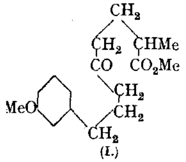
40. *Experiments on the Synthesis of Substances related to the Sterols. Part VIII. A Ketomethoxymethylhexahydrophenanthrene.*

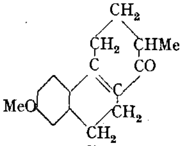
By Robert Robinson and James Walker.

The new hydrophenanthrene synthesis recorded in Part III (Robinson and Schlittler, J., 1935, 1288) involves a double ring-closure and in the final stage a β-arylethyldihydroresorcinol is dehydrated. In the example described in Part III, the course of the reaction was unambiguous, but the presence of a substituent in position 3 of the *cyclo*hexane ring allows of alternative courses.

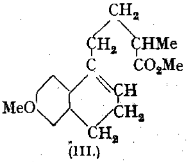
Employing methods similar to those of Part III, we obtained *methyl* 5-*keto*-8-m-*methoxyphenyloctane*-2-*carboxylate* (I), which was converted into a dihydroresorcinol derivative and then into 1-*keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10-*hexahydrophenanthrene* (II); this was, however, contaminated with a small proportion of a substance containing a CH_2·CO group, almost certainly the isomeric ketomethoxy-4-methylhexahydrophenanthrene.



(I.)



(II.)



(III.)

In order to be quite sure of the constitution of the ketone, we carried out the ring closures in a different sequence and obtained a dihydronaphthalene derivative (III) by the action of sulphuric acid on (I) at − 15°. The acid chloride related to (III) was then cyclised to (II) by an adaptation of Darzens' reaction. The ketone thus obtained was readily purified by crystallisation from methyl alcohol and, a seed having been acquired, the product of the first process mentioned above could also be crystallised; it proved to be identical with (II) and it was completely freed from the 4-methyl isomeride. The Darzens–Kipping reaction having served its turn, the method by way of the dihydroresorcinol is to be preferred for the preparation of (II).

Further work on (II) and its lower homologue, and especially on their dihydro-derivatives, is being actively prosecuted; the present record is necessitated by a publication of Cook and Lawrence (J., 1935, 1637), who also have employed the Darzens reaction in order to effect ring closure. At the time of writing their paper had been in our hands for a week, and we are thus taking the earliest opportunity to disclose our independent work in a similar direction.

Experimental.

Ethyl m-*Methoxycinnamate.*—*m*-Methoxybenzaldehyde (100 g.) was condensed with methyl acetate (Kindler and Peschke, *Arch. Pharm.*, 1932, **270**, 345). The crude product, containing some *m*-methoxycinnamic acid, was converted into the ethyl ester by refluxing in toluene or benzene with ethyl-alcoholic sulphuric acid; b. p. 172°/14 mm. (135 g.).

m-Methoxycinnamic acid is obtainable in high yield (> 90%) by condensation of *m*-methoxybenzaldehyde with malonic acid at 100° in the presence of pyridine with or without the addition of piperidine. Our experience in this case confirms the observations of Kurien and Pandya (*J. Indian Chem. Soc.*, 1934, **11**, 825) and Vahidy and Pandya (*Proc. Indian Acad. Sci.*, 1935, **2**, 402) that no excess of malonic acid is requisite and the pyridine employed may be restricted to 0·15 molar proportion.

Ethyl β-m-*Methoxyphenylpropionate.*—Ethyl *m*-methoxycinnamate (70 g.) in methyl alcohol (180 c.c.) along with 2% palladised strontium carbonate (12 g.) was shaken in hydrogen under an excess pressure of 2—3 atms. The requisite absorption of hydrogen took place in 12—20 minutes; the filtered solution was evaporated, and ethyl β-*m*-methoxyphenylpropionate isolated, b. p. 145—146°/10·5 mm. (68 g.).

An improvement in the preparation of γ-*m*-methoxyphenylbutyric acid consisted in the direct preparation of its nitrile from γ-*m*-methoxyphenylpropyl chloride with sodium iodide as catalyst.

Ethyl α-Acetyl-α'-methylglutarate.—Methyl α-methylacrylate and ethyl acetoacetate were condensed as described by Ruzicka (*Helv. Chim. Acta*, 1919, **2**, 153). The reaction mixture was added to much water, rendered just acid with acetic acid, and extracted with ether after saturation of the aqueous layer with sodium chloride. Replacement of methyl by ethyl occurred (Found: C, 58·6; H, 8·2. Calc. for $C_{12}H_{20}O_5$: C, 59·0; H, 8·2%). The ester, b. p. 147—150°/10 mm., was obtained in 25% yield, as found by Ruzicka.

Methyl γ-Acetyl-α-methylbutyrate.—Ethyl α-acetyl-α'-methylglutarate (46 g.) was hydrolysed as described by Bentley and Perkin (J., 1896, **69**, 1511) for the lower homologue and the crude acid was esterified with an ethereal solution of diazomethane (from 40 g. of nitrosomethylurea). The *ester* (27·2 g.; overall yield, 91%) distilled at 110—112°/24 mm. as a colourless mobile oil, $n_D^{18°}$ 1·4297 (Found: C, 60·8; H, 9·0. $C_8H_{14}O_3$ requires C, 60·8; H, 8·9%).

*Methyl 5-Keto-8-*m-*methoxyphenyloctane-2-carboxylate* (I).—A solution of γ-*m*-methoxyphenylbutyryl chloride (from 22 g. of the acid; cf. Robinson and Schlittler, *loc. cit.*) in dry benzene (80 c.c.) was added to one of methyl sodio-α-acetyl-α'-methylglutarate (from 27·5 g. of the ester and 2·6 g. of finely powdered sodium) in dry benzene (250 c.c.). The initially formed gel redissolved on standing and, after 15 hours at room temperature and 2 hours at the boiling point, the mixture was added to water and separated. The benzene solution was washed with sodium carbonate solution, dried (sodium sulphate), and evaporated. On acidification of the aqueous washings a small amount (*ca.* 2 g.) of *m*-methoxyphenylbutyric acid was recovered. The residual syrup (43 g.) was hydrolysed in the manner described by Robinson and Schlittler (*loc. cit.*). The crude hydrolysate (30 g.) from two experiments was esterified with an ethereal solution of diazomethane (from 30 g. of nitrosomethylurea) and fractionated. There were obtained: (i) 18·6 g., b. p. 130—170°/0·3 mm., which consisted of methyl γ-*m*-methoxyphenylbutyrate distilling mainly at 130—145°/0·3 mm., and (ii) 9·1 g., b. p. 170—200°/0·3 mm., a limpid, pale yellow oil (b. p. mainly 190—200°/0·3 mm.). The trace of halogen in

this material (Found : C, 67·5; H, 8·0%) was removed as follows : The *ester* (18·4 g.) in methyl alcohol (150 c.c.) was shaken with 2% palladised strontium carbonate (7 g.) for 2 hours in hydrogen under 1 atm. excess pressure. The solution was filtered from catalyst and concentrated, and the residue distilled; a halogen-free product (17·9 g.) was then obtained, b. p. 210°/1 mm., $n_D^{14.5°}$ 1·5082 (Found : C, 69·3; H, 8·1. $C_{17}H_{24}O_4$ requires C, 69·8; H, 8·2%).

1-*Keto-7-methoxy-2-methyl-*1 : 2 : 3 : 4 : 9 : 10-*hexahydrophenanthrene* (II).—(A) The above ester (I) (4·5 g.) in dry ether (25 c.c.) was treated at room temperature with alcohol-free sodium ethoxide (2 g.), a quick rise in temperature occurring; after 20 hours at room temperature the mixture was refluxed for an hour and added to ice-cold water. The alkaline aqueous solution was thrice extracted with small amounts of ether, acidified with sulphuric acid, and extracted with chloroform. On drying (sodium sulphate) and evaporation, the chloroform extract yielded a pale yellow syrup (3·9 g.), which turned into a white solid; this became sticky when kept over sulphuric acid in a vacuum and could not be satisfactorily crystallised. This dihydroresorcinol derivative was treated directly in the manner described by Robinson and Schlittler (*loc. cit.*) with phosphoric oxide in pure benzene which had jnst previously been shaken with water. On distillation of the crude product (2·6 g.) a pale yellow, viscous syrup (2·0 g.) was obtained, b. p. 175—180°/0·2 mm. This solidified in the ice-chest after a few days, but it contained, in addition to the desired product (II), a small amount of the 4-methyl isomeride, as was shown by the following experiment : A solution of the product (50 mg.) and β-resorcylaldehyde (35 mg.) in pure ethyl acetate (1 c.c.) was saturated with dry hydrogen chloride and kept for a few hours; a dark reddish-brown pyrylium salt separated. The salt dissolved in water to an orange solution with a bright orange fluorescence; it dissolved in concentrated sulphuric acid, giving a reddish-orange solution with an intense green fluorescence, and the anhydronium base dissolved in benzene to a deep bluish-red solution. A control experiment with resorcylaldehyde alone under the same conditions afforded no such pyrylium salt.

The product was pressed on porous porcelain and washed with chilled low-boiling light petroleum; it then had m. p. 63—65° (Found : C, 79·4; H, 7·6. $C_{16}H_{18}O_2$ reqnires C, 79·3; H, 7·4%). Recrystallisation was not effected until nucleation with the homogeneous material from the method B (see below) was practicable, and then the substance was readily separated from the trace of the 4-methyl isomeride by crystallisation from methyl alcohol; it was so obtained as hexagonal flat prisms, m. p. 67—68° alone or in admixture with the ketone derived from the experiment (B). The pure product gave a negative result in the β-resorcylaldehyde test described above.

(B) The ester (III) described below (4·0 g.) was refluxed with 10% methyl-alcoholic potassium hydroxide for 4 hours, and the acid isolated in the usual way and converted into the chloride by the action of thionyl chloride (1·06 c.c.; 1 mol.) in ether (20 c.c.) in the presence of pyridine (1·2 c.c.; 1 mol.) (cf. Carré and Libermann, *Compt. rend.*, 1934, **199**, 1422). The acid chloride, dissolved in carbon disulphide (12 c.c.), was added gradually to a solution of stannic chloride (1·7 c.c.; 1 mol.) in carbon disulphide (20 c.c.) cooled to − 10°. A blackish-brown granular complex was formed which later became reddish-brown and resinous. After 18 hours at room temperature, the complex was decomposed with ice-water, an emulsion being formed which was effectively separated after the addition of ether. The ether–carbon disulphide extract was dried and evaporated and the crude product was heated at 180° for 2 hours with a slight excess of dimethylaniline (3·5 c.c.), cooled, and treated with ether and dilute sulphuric acid. The ethereal solution was washed thrice with dilute sulphuric acid, twice with sodium carbonate solution, dried, and evaporated. The crude product (1·8 g.) was distilled, affording a pale yellow, viscous oil (1·5 g.), b. p. 175—183°/0·26 mm., which rapidly solidified (Found : C, 79·2; H, 7·5. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%). The substance separated from methyl alcohol in hexagonal flat prisms, m. p. 67—68°.

Crude acid (1 g.) (corresponding to III) was recovered from the sodium carbonate washings and by dissolving the pyridine hydrochloride in water and extracting the solution with ether.

The 2 : 4-*dinitrophenylhydrazone* separated when a hot concentrated solution of 2 : 4-dinitrophenylhydrazine and a concentrated solution of the ketone were mixed and cooled. It crystallised from ethyl acetate in bright red, felted needles, m. p. 221° (Found : N, 13·3. $C_{22}H_{22}O_5N_4$ requires N, 13·3%).

Methyl γ-6-Methoxy-3 : 4-dihydro-1-naphthyl-α-methylbutyrate (III).—Methyl 5-keto-8-*m*-methoxyphenyloctane-2-carboxylate (I) (15 g.) was dissolved in concentrated sulphuric acid (70 c.c.) at − 15°. The deep reddish-brown solution was kept in the freezing mixture for 3 hours and then poured on ice and extracted with ether. The extract was washed with sodium carbonate solution, dried (sodium sulphate), and evaporated. The product (11·2 g.) distilled

as a practically colourless, viscid oil (10·8 g.) at 181—183°/0·5 mm., $n_D^{18°}$ 1·5480 (Found: C, 74·3; H, 8·1. $C_{17}H_{22}O_3$ requires C, 74·4; H, 8·0%).

The authors thank the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship, and Imperial Chemical Industries Limited for grants. They are also grateful to Mr. J. Resuggan for assistance in the preparation of methoxyphenylbutyric acid.

The Dyson Perrins Laboratory, Oxford University. [*Received, December 11th*, 1935.]

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41. *The Preparation of Tetrahydrofurfuryl Bromide and its Reaction with Magnesium.*

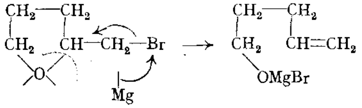
By Robert Robinson and Leonard Hart Smith.

The conversion of tetrahydrofurfuryl alcohol into the bromide has been studied by Dox and Jones (*J. Amer. Chem. Soc.*, 1928, **50**, 2033), Gilman and Brown (*Iowa State Coll. J.*, 1931, **6**, 11), and Paul (*Bull. Soc. chim.*, 1933, **53**, 421), the last claiming a yield of 50%. After many trials we have found conditions under which Paul's method can be employed for the preparation of the bromide in 58—62% yield consistently. Our further use of the reagent forms part of an investigation, an account of which we hope shortly to submit to the Society, but we now comment on the course of its reaction with magnesium.

According to Paul (*loc. cit.*), the reaction in dry ether proceeds normally with formation of a Grignard reagent and, on decomposition with water, tetrahydrosylvane is obtained in 45% yield (allowing for recovered bromide). On the other hand, if the ether is removed and the residue heated for 2 hours at 100—110°, Δ^4-penten-1-ol can be isolated in 50% yield after decomposition of the product with water.

We are unable to confirm this contrast, because in our experience the unsaturated alcohol is the main product when (*a*) highly purified anhydrous ether, (*b*) pure ether saturated with water, (*c*) unpurified ether, or (*d*) ether mixed with one-sixth of its volume of alcohol is used. In (*a*) the temperature was never higher than 50°; tetrahydrosylvane was only formed in traces, if at all, and the amount of recovered bromide was negligibly small (Paul recovered about 30%).

It would appear that hydroxylic compounds are not essential and the mechanism of this interesting decomposition * may be represented by the scheme:



This represents the magnesium as electron-donor to bromine; there are two less acceptable alternatives in which (*a*) the electrons are donated to oxygen, and (*b*) one electron passes from magnesium metal to bromine and one to oxygen.

Experimental.

Tetrahydrofurfuryl Bromide.—A mixture of tetrahydrofurfuryl alcohol (102 g.) and pyridine (5 c.c.) was added dropwise during 2·5—3 hours to one of phosphorus tribromide (96 g.) and pyridine (15 c.c.) with mechanical stirring and maintenance at 0°. Stirring was prolonged one hour, and the mixture kept in the bath until the temperature became that of the room. After 24 hours the almost colourless material was liquefied by cautious heating and distilled, b. p. 60—90°/13 mm.; on redistillation, b. p. 60—65° (nearly all at 61°)/13 mm., $n_D^{18°}$ 1·4880 (yield.

* The reaction appears to be analogous to that between β-phenoxyethyl bromide and magnesium (Grignard, *Compt. rend.*, 1904, **138**, 1048) which results in the formation of ethylene, phenol, and diphenoxybutane. Our own experiments confirm these observations, but we obtained in addition some phenetole, b.p. 173—174°, after decomposition of the product with water.

104 g. or 63%) (Found : Br, 48·1. Calc. for C_5H_9OBr : Br, 48·5%). The fraction of higher b. p. was isolated by collecting the first distillate at 60—135°/13 mm. (not recommended) or by steam-distilling the original reaction product after the addition of hydrobromic acid (100 c.c.; *d* 1·5), followed by fractionation. In this way 1 : 2 : 5-tribromopentane (*ca.* 5 g.), b. p. 132°/13 mm. (Paul, *loc. cit.*, gives 143°/20 mm.), was obtained (Found : C, 19·7; H, 3·0; Br, 77·4. Calc. for $C_5H_9Br_3$: C, 19·4; H, 2·9; Br, 77·8%).

Reaction with Magnesium.—(a) Reaction was initiated by the addition of a trace of iodine to a mixture of tetrahydrofurfuryl bromide (2 c.c.), magnesium turnings (2·4 g.), and absolute ether (15 c.c.); the remainder of the bromide (total, 16·5 g.), dissolved in dry ether (75 c.c.), was then added gradually so as to maintain a steady rate of reaction, and access of moisture was prevented. After 2 hours the mixture was heated during 3 hours to 40—45° and nearly all the magnesium passed into solution. The cooled product was decomposed with water and dilute hydrochloric acid. The separated and dried ethereal layer was fractionated through an efficient column (the vapour never rose above 37°) and finally a small Vigreux column. Only 0·7 g. was collected from 45—135° and the rise of b. p. was continuous (tetrahydrosylvane has b. p. 82°); the next fraction had b. p. 135—139° (nearly all at 136—137°/745 mm.) (5·3 g.); the amber-coloured residue (3·5—4·0 g.) partly crystallised.

(b) The reaction was initiated as in (a), the same quantities being used; the second portion (50 c.c.) of ether used was, however, previously shaken with water and separated. The reaction was very brisk and was completed at 60—70°. On working up, there were obtained 5·9 g., b. p. 52·5—53°/11 mm. or 137—138·5°/752 mm., and 0·3 c.c., b. p. 56—70°/11 mm.; the residue could not be distilled.

(c) Using ether from the reagent shelf in a similar experiment, completed by heating at 45—50°, we obtained 5·2 g., b. p. 136—138°/750 mm.

(d) The reaction was initiated between magnesium (4·8 g.) and tetrahydrofurfuryl bromide (5 g.) in absolute ether (40 c.c.) and continued by the addition of a mixture of the bromide (28 g.), ether (20 c.c.), and alcohol (10 c.c.); it was finally completed at 40—50°. We isolated 1·1 g., b. p. 85—91°, and 8·8 g., b. p. 135—137°.

The liquid, b. p. 135—137°, obtained in the above experiments contained a trace of halogen; this was removed by a process of refined fractionation (private communication of unpublished method) and then had b. p. 136°/750 mm., $n_D^{15.5}$ 1·4312 (Found : C, 69·1; H, 11·7. Calc. for $C_5H_{10}O$: C, 69·8; H, 11·6%). The phenylurethane had b. p. 183·5°/16 mm. Δ^4-Penten-1-ol has b. p. 138·5—139·5°/766 mm. (Paul, *Ann. Chim.*, 1932, **18**, 334), and its phenylurethane has b. p. 184°/16 mm. (Paul, *Compt. rend.*, 1931, **192**, 1575).

Tetrahydrofurfuryl bromide did not react with zinc filings in boiling absolute alcohol during 5½ hours.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, December 13th*, 1935.]

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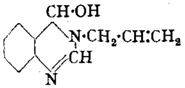
42. *Derivatives of Quinazoline.*

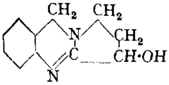
By (MISS) T. M. REYNOLDS and ROBERT ROBINSON.

THE constitution (I) was proposed by Späth and Nikawitz (*Ber.*, 1934, **67**, 45) for vasicine (peganine), but was later withdrawn (Späth, Kuffner, and Platzer, *Ber.*, 1935, **68**, 699). The formula did not commend itself to us for two reasons : (1) it is not in harmony with the chemical behaviour of vasicine; (2) vasicine is identical with " peganine," a congener of harmaline, but the structure (I) bears no relation to that of the alkaloids of the indole group. For the latter reason we synthesised (I) and found it to differ from vasicine in the anticipated way (compare *Nature*, 1934, **134**, 142). The true constitution (II) of vasicine has now been elucidated by the work of Rây, Späth, Adams, and their several collaborators, and it is seen that the N·C·C·C·N group characteristic of the ornithine series of amino-acids and alkaloids is present in the molecule. The fact that Späth's first formula (I) could not be reconciled with a view of the biogenesis of *harmala* alkaloids which has been put forward in several places by one of us is a sufficient explanation of our interest in the matter. But, as Professor Späth has protested (*Ber.*, 1935, **68**, 938) that we had no right to perform our very simple experiment, we find it necessary to point out that the field of study in question, if reserved at all, was the preserve of Ghose and Rây and their colleagues

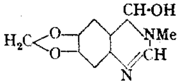
and we were favoured by some private discussions with Professor J. N. Rây on the subject of vasicine at a time when he was travelling in Europe. Professor Rây's views on



(I.)



(II.)



(III.)

Späth's formula were identical with our own, but he, being separated from his laboratory, was unable to apply the obvious crucial test himself.

Having obtained (I), we took the opportunity to examine the extent of its analogy with carbinol-amines of the *iso*quinoline series and prepared the hydrastinine analogue (III) with the same object. The quinazoline carbinol-amines do not closely resemble cotarnine and hydrastinine, although some similar condensations are recorded below.

Experimental.

3-*Allylquinazolinium Iodide*.—A cold mixture of quinazoline (4 g.), allyl iodide (4 c.c.), and ethyl acetate (5 c.c.) was kept for 12 hours and the resulting crystalline mass (3·8 g.) was collected and washed with ethyl acetate. The bright yellow product dissolved freely in alcohol and was precipitated as an oil by the addition of ethyl acetate, benzene, or ether. When rubbed with ether, the oil crystallised and the specimen (m. p. 104—107°) used for analysis was triturated thoroughly with ethyl acetate to remove coloured impurities (Found: C, 44·6, 44·6; H, 4·4, 4·3; N, 9·3. $C_{11}H_{11}N_2I,0{\cdot}33C_2H_6O$ requires C, 44·7; H, 4·2; N, 9·0%). The presence of alcohol was qualitatively confirmed. A further quantity of the *iodide* separated from the ethyl acetate mother-liquor and after 48 hours an almost quantitative yield was obtained.

4-*Hydroxy*-3-*allyl*-3 : 4-*dihydroquinazoline* (I).—A mixture of 3-allylquinazolinium iodide (5 g.), water (15 c.c.), and an excess of freshly precipitated silver chloride was shaken for 30 minutes, the liquid filtered, and the silver salts washed with cold water. The combined filtrate and washings (*ca.* 30 c.c.) were cooled to 0° and potassium hydroxide solution (5 c.c. of 33%) was gradually added. The liquid clouded, then cleared, and after a few minutes a colourless solid began to separate; this was collected (1·8 g.) after 30 minutes and recrystallised from benzene; m. p. 130—131° (Found: C, 70·4; H, 6·4; N, 14·6. $C_{11}H_{12}ON_2$ requires C, 70·2; H, 6·4; N, 14·9%). The substance is easily decomposed by cold alkali and it is essential to observe the prescribed conditions for its preparation. An oily, ether-soluble, diazotisable amine is formed when 4-hydroxy-3-allyl-3 : 4-dihydroquinazoline is heated with dilute aqueous alkali. The carbinol-amine is also decomposed by heating with water and, except in small quantities, cannot be recrystallised in this way; it is alkaline to litmus. It is easily soluble in alcohol and in acetone and is recovered unchanged by evaporation of the solutions at their boiling point or at room temperature in a desiccator, and it does not react with acetone in the presence of saturated aqueous sodium carbonate.

3-*Allylquinazolinium Picrate*.—When cold aqueous picric acid (1%) was added to a solution of 3-allylquinazolinium chloride, prepared as described above, a bright yellow picrate separated as a quickly solidifying oil. It crystallised from alcohol in plates, m. p. 124° after sintering (Found: C, 51·4; H, 4·4; N, 15·8; loss in a high vacuum at 104°, 10·3. $C_{17}H_{13}O_6N_5,C_2H_6O$ requires C, 51·2; H, 4·3; N, 15·7; C_2H_6O, 10·3%).

The addition of cold saturated aqueous picric acid to an alcoholic solution of 4-hydroxy-3-allyl-3 : 4-dihydroquinazoline afforded the same picrate (m. p. and undepressed mixed m. p.).

4-*Nitromethyl*-3-*allyl*-3 : 4-*dihydroquinazoline Picrate*.—A solution of 4-hydroxy-3-allyl-3 : 4-dihydroquinazoline (0·2 g.) and nitromethane (0·7 c.c.) in alcohol (1·5 c.c.) was gently heated on a steam-bath for 5 minutes and then evaporated, leaving an almost colourless oil which did not crystallise. The residue was dissolved in a little alcohol, and cold aqueous picric acid (1%) added, precipitating an oily *picrate*, which eventually crystallised and separated from alcohol in prisms, m. p. 152—153° (Found: C, 47·0; H, 3·6. $C_{18}H_{16}O_9N_6$ requires C, 47·0; H, 3·5%).

4-*Nitromethyl*-3-*methyl*-3 : 4-*dihydroquinazoline*.—A solution of 4-hydroxy-3-methyl-3 : 4-dihydroquinazoline (0·2 g.) and nitromethane (1 c.c.) in alcohol (2 c.c.) was kept for 24 hours, then concentrated, and a yellow crystalline solid precipitated by ether. The *substance* crystal-

lised from benzene–light petroleum in prismatic needles, m. p. 137° (Found : C, 58·8; H, 5·4. $C_{10}H_{11}O_2N_3$ requires C, 58·5; N, 5·3%).

6-Nitropiperonylidenediformamide.—A mixture of formamide (100 c.c.), 6-nitropiperonal (60 g.), and benzene (150 c.c.) was heated to 60° and then stirred vigorously without further heating while a rapid stream of dry hydrogen chloride was passed. Crystals soon separated and after 1·5—2 hours the liquid could no longer be stirred; at the same time the temperature, which had remained sensibly constant at 50°, quickly rose to 80—85°. After 3 hours the benzene layer was decanted and the semi-solid mass was washed with hot benzene, then mixed with alcohol, and filtered. After being washed successively with alcohol, 50% aqueous alcohol, and water, the solid was triturated thoroughly with cold aqueous sodium hydroxide (5%), collected, and washed with sodium hydroxide solution and water, leaving pale yellow crystals (28 g.). The benzene layer and washings were combined, heated to 60° with formamide (50 c.c.), and treated in the same way, yielding a further quantity (13 g.) of *6-nitropiperonylidenediformamide.* The substance was almost insoluble in non-hydroxylic solvents and crystallised from water as light yellow needles, m. p. 248—250° (decomp.) after sintering (Found : C, 45·2; H, 3·2; N, 15·6. $C_{10}H_9O_6N_3$ requires C, 44·9; H, 3·4; N, 15·7%).

Acidification of the alkaline extracts afforded a cream-coloured amorphous solid (*ca.* 20 g.), the nature of which has not been determined. Variations of the above procedure led in most cases to an increase in the amount of this by-product or to incomplete reaction.

6 : *7-Methylenedioxyquinazoline.*—Crushed ice (180 g.) and glacial acetic acid (60 g.) were slowly added to a mixture of finely powdered 6-nitropiperonylidenediformamide (15 g.) and zinc dust (45 g.) with vigorous shaking. After 30 minutes the mixture was mechanically stirred for 1·5 hours, during which small quantities of zinc dust were frequently added; the maximum temperature reached was 50°. The mixture was filtered, and aqueous sodium hydroxide (300 c.c. of 50%) added to the filtrate with cooling. After dissolution of the precipitated zinc hydroxide the crystalline methylenedioxyquinazoline was collected, dried, and crystallised from ethyl acetate and then from water, forming colourless plates (6 g.), m. p. 171—172° (Found : C, 62·0; H, 3·5; N, 16·2. Calc. for $C_9H_6O_2N_2$: C, 62·1; H, 3·4; N, 16·1%). Wilkendorff (*Ber.*, 1919, 52, 609) gives m. p. 172—173° after distillation. 6 : 7-Methylenedioxyquinazoline is easily soluble in hot ethyl acetate, acetone, water, and ether and in cold chloroform and benzene; less readily soluble in light petroleum.

When the reaction mixture was filtered and basified after being shaken for 1 hour, the temperature not being allowed to rise above 15°, as in the preparation of quinazoline, a mixture of substances was obtained. The product was much less soluble in ethyl acetate and the first fraction which separated was a pale-coloured, weak, non-diazotisable *base.* This was recrystallised from alcohol; m. p. 260—261° (Found : C, 57·2; H, 3·1; N, 14·9. $C_9H_6O_3N_2$ requires C, 56·8; H, 3·2; N, 14·7%). The second fraction was a mixture, and the third almost pure 6 : 7-methylenedioxyquinazoline.

6 : *7-Methylenedioxy-3-methylquinazolinium Iodide.*—A mixture of methyl iodide (5 c.c.), 6 : 7-methylenedioxyquinazoline (4 g.), and ethyl acetate (75 c.c.) was gently refluxed for 10 hours. Shining yellow plates separated (7 g.); recrystallised from alcohol, they had m. p. 239—240° after sintering (Found: C, 38·5; H, 3·0; N, 8·6. $C_{10}H_9O_2N_2I$ requires C, 38·0; H, 2·8; N, 8·9%).

4-Hydroxy-6 : 7-methylenedioxy-3-methyl-3 : 4-dihydroquinazoline (III).—Finely powdered 6 : 7-methylenedioxy-3-methylquinazolinium iodide (7 g.) and an excess of freshly prepared silver chloride were shaken with water (12 c.c.), the liquid filtered, and the silver salts washed with water. The combined filtrate and washings (*ca.* 20 c.c.) were cooled to 2°, and potassium hydroxide solution (2 c.c. of 50%) added. The temperature rose to 10°, the solution became orange and then yellow, and after a few minutes a pale brown oil separated and crystallised on rubbing. After cooling in ice-water for 15 minutes, the solid was collected (3 g.) and crystallised by addition of water (2—3 vols.) to its solution in hot alcohol (charcoal). The *substance* separated as colourless, flat, diamond-shaped prisms, m. p. 158—159° with evolution of gas, after softening at 154° (Found : C, 58·5; H, 5·0; N, 13·3. $C_{10}H_{10}O_3N_2$ requires C, 58·2; H, 4·8; N, 13·6%). Its solution in concentrated sulphuric acid is pale yellow and after a few minutes becomes light green with a bright pink fluorescence. The solutions in dilute acids are non-fluorescent (cf. the bright fluorescence of hydrastininium salts).

Methylenedioxymethylquinazolinium picrate was obtained by the addition of cold aqueous picric acid (1%) to a solution of the carbinol base in aqueous alcohol (50%), and crystallised from alcohol, in which it was sparingly soluble; m. p. 185—186° after softening at 183° (Found : C, 46·2; H, 2·8. $C_{16}H_{11}O_9N_5$ requires C, 46·0; H, 2·6%).

When hydroxydihydromethylenedioxymethylquinazoline was boiled with aqueous sodium hydroxide (2%) for 30 seconds, the solution became yellow and deposited an oil, which solidified, on cooling, as pale yellow needles. These were recrystallised once from aqueous alcohol and identified by m. p. and undepressed mixed m. p. as 6-aminopiperonal. [6-Aminopiperonal dissolved when warmed in the steam-bath for 10 minutes with aqueous methylamine (33%), and a colourless solid separated; this was collected and washed with water, m. p. 108—109°, mixed with 6-aminopiperonal, m. p. 75—80°. The condensation product was resolved into 6-aminopiperonal and methylamine during recrystallisation from water or 50% alcohol.]

6 : *7-Methylenedioxy-4-nitromethyl-3-methyl-3 : 4-dihydroquinazoline.*—A solution of nitromethane (0·7 c.c.) and hydroxymethylenedioxymethyldihydroquinazoline (0·5 g.) in alcohol (1·5 c.c.) was kept at room temperature for 24 hours, then concentrated to small bulk, and the residue cooled; a bright yellow, crystalline solid separated on the addition of ether. The *substance* was readily soluble in alcohol and ethyl acetate, but less freely soluble in benzene, from which it crystallised in clusters of small prisms, m. p. 159—160° after sintering (Found : C, 53·1; H, 4·2; N, 16·7. $C_{11}H_{11}O_4N_3$ requires C, 53·0; H, 4·4; N, 16·9%).

4-Acetonyl-6 : 7-methylenedioxy-3-methyl-3 : 4-dihydroquinazoline Picrate.—Saturated aqueous sodium carbonate was added to a solution of hydroxymethylenedioxymethyldihydroquinazoline (0·2 g.) in acetone (3 c.c.) and the mixture was shaken for about 30 minutes and then at intervals during 2 days. The liquid was then filtered, and water added to the concentrated filtrate. The oil which separated could not be crystallised; it was converted into a *picrate*, which crystallised from alcohol; m. p. 187° after sintering from 184° (Found : C, 48·0; H, 3·8. $C_{19}H_{17}O_{10}N_5$ requires C, 48·0; H, 3·7%).

The authors thank the Royal Commissioners for the Exhibition of 1851 for an Overseas Studentship awarded to one of them.

The Dyson Perrins Laboratory, Oxford University. [*Received, December 13th*, 1935.]

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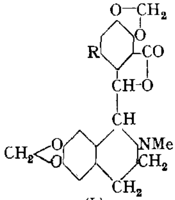
43. *Synthesis of Bicuculline. Part I.*

By P. W. G. Groenewoud and Robert Robinson.

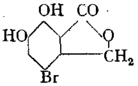
Development in the phthalide section of the *iso*quinoline group of the alkaloids appeared in recent years to have been arrested until the appearance of papers by R. H. F. Manske announcing the discovery of new members of the group in certain *Fumariaceae*.

Bicuculline (I, R = H) was first encountered as a constituent of *Dicentra cucullaria* (Manske, *Canadian J. Research*, 1932, 7, 265) and subsequently found in *Corydalis sempervirens*, *Adlumia fungosa*, and *Corydalis aurea* (Manske, *ibid.*, 1933, **8**, 210, 407; **9**, 436). The constitution of the base was deduced from its character as a lactone and from the formation of hydrastinine and 2-carboxy-3 : 4-methylenedioxybenzaldehyde on oxidation.

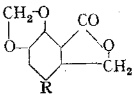
The present memoir describes the synthesis of inactive bicuculline, and Part II, in collaboration with Dr. Manske, will deal with its stereochemical relations. We may anticipate Part II to the extent of stating that the inactive synthetic material has been resolved and the *d*-base proved identical with bicuculline.



(I.)



(II.)



(III.)

The methylenedioxyphthalide (III, R = H) required for the synthesis according to the

methods of Hope and Robinson (J., 1911, **99**, 1153) and Hope, Pyman, Remfry, and Robinson (J., 1931, 236) was prepared by Perkin and Trikojus (J., 1926, 2925) from *o*-veratraldehyde by a series of processes, but we preferred a new method based on the observation of Robinson and Streight that bromomeconin can be demethylated (J., 1934, 1130).

Bromonormeconin (II) was found to be difficult to methylenate, but this was eventually effected in 45% yield by the use of methylene sulphate (cf. Baker, J., 1931, 1765); the product (III, R = Br) was debrominated by means of hydrazine and palladised strontium carbonate (Busch, *Z. angew. Chem.*, 1925, **38**, 519) or equally conveniently by means of zinc dust and boiling aqueous sodium hydroxide.

3 : 4-Methylenedioxyphthalide is readily converted into its 6-*nitro*-derivative (III, R = NO_2) and the facile condensation of the latter substance with cotarnine follows the usual course.

Coupling with lodal (Pyman, J., 1909, **95**, 1266) [carbinolamine related to 4 : 5-dimethoxy-2-(β-methylaminoethyl)benzaldehyde] furnished *nitro*-x-*adlumine*,* which it is hoped may be transformed into adlumine (Manske, *Canadian J. Research*, 1933, **8**, 210). The laudanosine necessary for the preparation of lodal was obtained in 90% yield by catalytic reduction of papaverine methochloride.

6-Nitro-3 : 4-methylenedioxyphthalide and hydrastinine afforded *nitro*-x-*bicuculline* (I, R = NO_2) in favourable yield and the usual methods were applied for the conversion of this base into *amino*-x-*bicuculline* and then into *iodo*-x-*bicuculline* and x-*bicuculline*. This route was selected in preference to the alternative through the hydrazino-derivative.

Experimental.

6-*Bromo*-3 : 4-*methylenedioxyphthalide* (III, R = Br).—Many unsuccessful or partly successful trials were made with methylene bromide or methylene iodide under various conditions for the methylenation of bromonormeconin. The following directions should be followed closely. A solution of sodium hydroxide (3·3 g.) in water (100 c.c.) was added to one of bromonormeconin (10·0 g.) in acetone (100 c.c.) (oxygen-free nitrogen atmosphere), and the mixture gently refluxed. Methylene sulphate (32·0 g.) and sodium hydroxide (19·6 g. in 75 c.c. of water) were then added alternately and in small portions with continued heating and vigorous stirring during 1 hour. Stirring was continued for 15 minutes; hydrochloric acid was then added in excess, and the acetone removed by distillation under diminished pressure. The acid solution was boiled and cooled, and the sticky solid collected. It was lixiviated with alcohol and the grey powder which remained was collected and dried (4·65 g. or 44%); bromonormeconin was recovered from the alcoholic solution. 6-*Bromo*-3 : 4-*methylenedioxyphthalide* crystallises from ethyl alcohol or acetic acid in white flakes, m. p. 196° (Found : C, 42·2; H, 2·1. $C_9H_5O_4Br$ requires C, 42·0; H, 2·0%); it is very sparingly soluble in cold alcohol or ether and it exhibits the behaviour of a lactone.

3 : 4-*Methylenedioxyphthalide*.—(A) Reduction of the bromo-derivative by means of aluminium amalgam in boiling alcoholic solution gave methylenedioxyphthalide in 73% yield. Perkin and Trikojus (*loc. cit.*) gave m. p. 227°, which was confirmed by Späth and Holter (*Ber.*, 1927, **60**, 1891). Manske (*Canadian J. Research*, 1933, **8**, 142) attributed the m. p. 234° to the substance, and in agreement we find m. p. 233—234° (Found : C, 60·7; H, 3·5. Calc. for $C_9H_6O_4$: C, 60·7; H, 3·5%).

The method was unsatisfactory when the scale of the operation was enlarged or when the bromo-derivative was not quite pure. The methods (B) and (C) are equally efficacious.

(B) A mixture of bromomethylenedioxyphthalide (4·0 g.), aqueous sodium hydroxide (150 c.c. of 10%), and zinc dust (10·0 g.) was refluxed for 8 hours; after cooling to 65°, filtration, and acidification, pure methylenedioxyphthalide (2·45 g. or 90%) separated.

(C) Bromomethylenedioxyphthalide (2·0 g.) was dissolved in the minimum of hot alcohol, and palladised strontium carbonate (4·0 g. of 2%), alcoholic potassium hydroxide (20 c.c. of 10%), and hydrazine hydrate (2·5 c.c.) added. The mixture was refluxed for 1 hour, filtered, concentrated, and acidified (yield, 1·2 g. or 86%).

6-*Nitro*-3 : 4-*methylenedioxyphthalide*.—Methylenedioxyphthalide (1·0 g.) was added portionwise to nitric acid (16 c.c., *d* 1·42), cooled in ice hut allowed such a rise of temperature as to

* The *x* signifies that the allocation to the stereoisomeric series α and β has not yet been carried out.

ensure complete solution before crystallisation of the product began. The mixture was kept for 15 minutes at 0° and for 1 hour at room temperature, and after addition of water the yellow flocculent precipitate was collected (1·15 g. or 92%). The very sparingly soluble *substance* crystallised from much alcohol and from acetic acid in pale yellow tablets, m. p. 222—223° (Found: C, 48·2; H, 2·1; N, 6·5. $C_9H_5O_6N$ requires C, 48·4; H, 2·2; N, 6·3%). It is soluble in boiling aqueous alkali to a bright red solution and is recovered very slowly on acidification and heating. On exposure to light the substance becomes dark yellow.

Anhydrocotarnine-6-nitro-3 : 4-methylenedioxyphthalide.—Cotarnine (2·2 g.) was added to a boiling solution and suspension of nitromethylenedioxyphthalide (2·0 g.) in alcohol (150 c.c.); a clear orange solution was quickly formed. The product crystallised in less than a minute and after boiling for 20 minutes the mixture was cooled and the solid collected (3·1 g. or 78%). The *base* is readily soluble in chloroform and crystallises from chloroform–methyl alcohol as small yellow leaflets, m. p. 177—178° (Found: C, 56·8; H, 4·1; N, 6·5. $C_{21}H_{18}O_9N_2$ requires C, 57·0; H, 4·1; N, 6·3%). The base is readily soluble in hydrochloric acid to a bright yellow solution; it is decomposed into its generators on boiling with acetic acid.

Anhydrocotarnine-6-amino-3 : 4-methylenedioxyphthalide.—A solution of crystallised stannous chloride (6·0 g.) in concentrated hydrochloric acid (7 c.c.) was added to an ice-cold mixture of anhydrocotarninenitromethylenedioxypbthalide (1·0 g.), acetic acid (6 c.c.), and granulated tin (1·0 g.). The temperature was allowed to rise to 15—18° and crystallisation of the double tin salt commenced after 20 minutes. After 5 hours, enough water to dissolve the salts was added and the base, liberated by means of a large excess of potassium hydroxide, was extracted with chloroform. The dried chloroformic solution was evaporated nearly to dryness, methyl alcohol added to the residue, and the liquid again distilled in order to remove chloroform. This process was twice repeated and the very pale yellow crystals were then collected (0·71 g. or 70%). The *base* crystallised from chloroform–methyl alcohol as tiny rods, m. p. 204—205° (decomp.) (Found: C, 60·2; H, 5·3; N, 6·9. $C_{21}H_{20}O_7N_2$,0·5MeOH requires C, 60·3; H, 5·1; N, 6·5%). It resembles closely amino-β-gnoscopine in its behaviour with solvents and in its diazotisability.

Laudanosine.—Platinum oxide (from 1·0 g. of chloroplatinic acid; "Organic Syntheses," VIII, 92) was added to a solution of papaverine methochloride (18·0 g.) in 70% aqueous alcohol (75 c.c.), which was then shaken with hydrogen (2000 c.c. absorbed at approximately 900 c.c. per hour). The solution was filtered through charcoal, concentrated, and mixed with water (350 c.c.), and sodium carbonate (2·0 g.) added. The crude precipitated base had m. p. 111° (pure, m. p. 115°) and after crystallisation from 50% aqueous alcohol was obtained as feathery needles (14·8 g. or 92%).

Anhydrolodal-6-nitro-3 : 4-methylenedioxyphthalide (Nitro-x-adlumine).—Lodal was prepared by the method of Pyman (*loc. cit.*) and also by synthesis using prescriptions of Kindler and Peschke (*Arch. Pharm.*, 1932, **270**, 350). Under the usual conditions, lodal (3·0 g.) and nitromethylenedioxyphthalide (2·0 g.) in alcohol (200 c.c.) afforded pale orange crystals (3·4 g. or 85%) of *nitro-x-adlumine*. This resembles other substances of its class and crystallises from chloroform–methyl alcohol in orange rectangular plates, m. p. 180—181° (decomp.) (Found: C, 59·0; H, 4·9; N, 6·1. $C_{21}H_{20}O_8N_2$ requires C, 58·9; H, 4·7; N, 6·5%). The base is more than usnally phototropic, becoming dark red when exposed to light and air for 2 hours. The reduction of the base was carried out as described above in the case of anhydrocotarninenitromethylenedioxyphthalide; the *amino*-derivative crystallised very slowly from chloroform–methyl alcohol as bundles of small needles, m. p. 218—219° (Found: C, 63·0; H, 5·6; N, 6·8. $C_{21}H_{22}O_6N_2$ requires C, 63·3; H, 5·5; N, 7·0%).

Nitro-x-bicuculline (I, R = NO_2).—Hydrastinine (10·5 g.) was added to a boiling solution and suspension of nitromethylenedioxyphthalide (11·5 g.) in ethyl alcohol (300 c.c.). The solution immediately assumed an orange-red colour and the nitro-compound had almost disappeared when the orange-red crystals of the condensation product made their appearance in the solution. The mixture was refluxed for 30 minutes, then cooled, and the product collected after a few hours (15·5 g. or 73%). Some nitromethylenedioxyphthalide was recovered from the mother-liquor. The *nitrobicuculline* is sparingly soluble in methyl and ethyl alcohols, but dissolves freely in acetone or chloroform. It can be conveniently crystallised from chloroform–methyl alcohol, separating in minute yellow needles, which sinter at 176° and blacken at 179° without exhibiting a definite m. p. (Found: C, 58·1; H, 4·2. $C_{20}H_{16}O_8N_2$ requires C, 58·3; H, 3·9%). The base can be recovered by the addition of ammonia to its yellow solution in dilute hydrochloric acid, but it is rapidly decomposed into its generators on heating with acetic acid.

Amino-x-bicuculline (I, R = NH_2).—Under the usual conditions of reaction and isolation, nitro-*x*-bicuculline (3·0 g.), acetic acid (18 c.c.), granulated tin (2·0 g.), hydrated stannous chloride (17·0 g.), and concentrated hydrochloric acid (19 c.c.) afforded a pale yellow, crystalline product, separating eventually from methyl alcohol (yield, 1·8 g. or 65%). This ***amino-x-bicuculline*** crystallises from mixtures of chloroform and methyl alcohol in flat, pale yellow prisms, m. p. 203—204° to a brown liquid (Found: C, 62·8; H, 5·0; N, 7·5. $C_{20}H_{18}O_6N_2$ requires C, 62·8; H, 4·7; N, 7·3%). The substance can be readily diazotised and coupled with β-naphthol to a crimson azo-compound.

Iodo-x-bicuculline (I, R = I).—Aqueous sodium nitrite was carefully added to a solution of amino-*x*-bicuculline (1 g.) in concentrated hydrochloric acid (12 c.c.) at 0° until a drop of the liquid after dilution was found to contain free nitrous acid. The solution became bright orange and a crystalline substance, presumably the diazonium chloride, separated. The mixture was diluted with water (30 c.c.) and gradually added to a solution of potassium iodide (8·0 g.) in water (150 c.c.) with vigorous stirring. After 10 minutes the iodine liberated was reduced by sulphurous acid and the *base* was collected (1·2 g. or 93%) after it had been liberated by means of ammonia. The colourless base is sparingly soluble in the simple alcohols and ether and crystallises from ethyl acetate or from chloroform–methyl alcohol as stout transparent prisms, m. p. 208—209° (Found: C, 48·5; H, 3·5; N, 3·1. $C_{20}H_{16}O_6NI$ requires C, 48·7; H, 3·3; N, 2·8%).

x-*Bicuculline* (*Anhydrohydrastinine*-3 : 4-*methylenedioxyphthalide*) (I, R = H).—A solution of iodo-*x*-bicuculline (0·6 g.) in ethyl alcohol (38 c.c.) and benzene (12 c.c.) was refluxed with an excess of amalgamated aluminium foil for 3 hours. The solvents were removed from the filtrate under diminished pressure, and the residue crystallised from chloroform–methyl alcohol (charcoal) (yield, 0·3 g. or 66% of halogen-free material). The *base* was obtained as colourless elongated plates, m. p. 215° (Found: C, 65·4; H, 4·6; N, 4·0. $C_{20}H_{17}O_6N$ requires C, 65·4; H, 4·6; N, 3·8%), sparingly soluble in the simple alcohols and ether, moderately readily soluble in benzene and ethyl acetate, readily soluble in chloroform.

The addition of ammonia or sodium hydroxide to a cold solution in dilute hydrochloric acid precipitates the base, but when the acid solution is added to hot aqueous sodium hydroxide, no precipitate is obtained owing to fission of the lactone ring. On acidification of the solution and heating, followed by cooling and addition of cold aqueous sodium hydroxide, the base is precipitated. The greenish-yellow solution in concentrated sulphuric acid becomes red and then dull purple on heating.

Derivatives of the base will be described in Part II.

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44. *Electrolytic Reduction of Organic Compounds. Part I. Analogies between Cathodic Reduction and the Action of Dissolving Metals. Reduction of Sorbic Acid.*

By ELIAS ISAACS and CHRISTOPHER L. WILSON.

BURTON and INGOLD (J., 1929, 2022) have suggested a theory to explain the process of reduction of an olefinic double bond by metals dissolving in suitable media. The scheme involves the successive addition to the unsaturated system of a proton together with two electrons supplied by the dissolving metal, and a second proton. The theory explains the susceptibility of Δ^{α}-unsaturated acids or ketones to attack by this type of reducing agent and enables the principles of prototropy to be applied in order to predict the orienting effects of substituents in the reduction of certain butadiene acids.

Illustrating their case by sorbic acid (I), Burton and Ingold argued that the second proton would be preferentially attached at that point in the ion (II) at which the electron density was the higher. Since by this theory the ratio of the amounts of the two dihydro-compounds is essentially determined by structure, it should be independent of the reducing system employed. These authors stated that they had intended to investigate quantitatively the reduction of sorbic acid by a variety of dissolving metals, the object being to vary the ease of access of electrons to the organic molecule. This project was, however,

frustrated by experimental difficulties and satisfactory results were obtained with only sodium and aluminium amalgams.

$$\text{(I.)}\ CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H \xrightarrow{H^+, 2e} CH_3{\cdot}\overset{\ominus}{\overbrace{CH{\cdot}CH{\cdot}CH}}{\cdot}CH_2{\cdot}CO_2H\ \text{(II.)} \xrightarrow{H^+}$$

$$CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \qquad CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$$

Although we also have not been able to extend Burton and Ingold's experiments in this direction, we have investigated the electrolytic reduction of sorbic acid and of the sorbate ion at a variety of metallic cathodes. We have shown that the hexenoic acids produced consist only of the Δ^{β}- and the Δ^{γ}-isomeride in relative amounts which are in each case characteristic of the unsaturated entity to within the range and accuracy of our experiments. This ratio, moreover, as will be evident from the table, is substantially equal to that which has been obtained in reductions by aluminium and sodium amalgams.

Δ^{γ}-Hexenoic Acid (%) in "Hydrosorbic" Acid.

	Medium : Aqueous			
Reducing agent.	NaOH.	$NaHCO_3$.	$CH_3{\cdot}CO_2H$.	H_2SO_4.
Hg cathode	40	41	54	52
Cd ,, ...	39	—	54	—
Cu ,, ...	40	—	50	—
NaHg *	—	40	55	—
AlHg *	45	45	—	—

* Burton and Ingold, *loc. cit.*; cf. Evans and Farmer, J., 1928, 1644; Goldberg and Linstead, *ibid.*, p. 2343.

This result is immediately intelligible in the case of the mercury cathode at least, if it is assumed that the electrical conditions obtaining at the cathode when evolving hydrogen are the same as those at the mercury surface of dilute sodium amalgam in the same medium, the sodium furnishing by its solution pressure the necessary cathodic potential. Such a view implies that all reactive amalgams should behave similarly, and excludes the idea of the intermediate addition of sodium or other metal atoms to the double bond (cf. Willstätter, Seitz, and Bumm, *Ber.*, 1928, **61**, 871). In support of this contention we have shown that anthracene can be reduced to the 9 : 10-dihydro-compound by sodium, aluminium, and magnesium amalgams and also at a mercury cathode in an alcoholic solution of sodium hydroxide, ammonium sulphate and ammonia, and tetramethylammonium hydroxide : one can hardly suppose that all these metals and quasi-metals like ammonium are added to the hydrocarbon.

The results for sorbic acid suggest an equivalence in mechanism between reduction by the reagents considered by Burton and Ingold and reduction at cathodes, a conclusion which is supported by many recorded observations. Comment has been passed on the similarities between the action of a mercury or lead cathode and dilute sodium amalgam in the reduction of Δ^{α}-double bonds (Marie, *Compt. rend.*, 1903, **136**, 1331; "Organic Syntheses," 1929, **9**, 42; Law, J., 1912, **101**, 1016); and between a lead cathode and sodium-lead alloy in the reduction of many substituted acetoacetic esters and quaternary ammonium salts (Fichter and Stenzl, *Helv. Chim. Acta*, 1933, **16**, 571; 1934, **17**, 669). We would stress also the great similarity of the behaviour of lead and mercury cathodes, and of dissolving metals and amalgams in the nuclear and the side-chain reduction of aromatic acids and esters (Aschan, *Ber.*, 1891, **24**, 1864; Weil, *Ber.*, 1908, **41**, 4147; Tafel aud Friedrichs, *Ber.*, 1904, **37**, 3187; Mettler, *Ber.*, 1905, **38**, 1745 *et seq.*). Even more striking is the electrolytic analogue of Clemmensen's method of reduction : the carbonyl group may successfully be reduced to a methylene group in strongly acid solutions at cathodes of cadmium, lead, mercury and even amalgamated zinc (Schepss, *Ber.*, 1913, **46**, 2564; Swann and Feldmann, *Trans. Amer. Electrochem. Soc.*, 1935, **67**, 195; Shima, *Mem. Coll. Sci. Kyoto*, 1929, *A*, **12**, 73).

Although the practical value of the electrolytic method is limited to reductions involving a fairly highly conducting catholyte, the process, nevertheless, has the advantage of permitting the employment of many different metallic cathodes, of which one may be much more efficient than another. Mercury, for instance, either as cathode or as amalgam, reduces sorbic acid to mixtures which always contain considerable proportions of pinacol-like " bimolecular " compounds. This behaviour appears to be a peculiarity of mercury, since copper and cadmium, which of course cannot be employed as dissolving metals, produce, as cathodes, smooth dihydrogenation of this acid.

In our experiments very little reduction was observed at a tin cathode and none at lead, smooth nickel, and shiny platinum. We were careful to bear in mind Tafel's injunctions (*Ber.*, 1900, **33**, 2209) concerning the adverse influence of impurities on the reducing efficiency of a lead cathode; our sample (purchased from A. Hilger, Ltd.) was guaranteed to contain less than 0·001% of foreign metals, and in spite of that it failed completely.

It has been suggested (cf. Brockman, " Electro-organic Chemistry," 1926, p. 275) that the magnitude of the hydrogen overvoltage of a cathode is an important factor in the electrolytic reduction of Δ^{α}-double bonds. This idea does not agree with our experiments, which indicate a reducing efficiency according to the series Cu, Hg $>$ Cd $\gg$ Sn $>$ Pt, Ni (smooth). On the other hand, hydrogen overvoltage seems important for the reduction of aliphatic and aromatic aldehydes and aliphatic ketones to hydrocarbons (cf. the above remarks on the Clemmensen reduction and its electrolytic counterpart).

The remarks made by Ingold and Rogers (J., 1935, 719) when discussing the peculiarities of amalgams in reduction may satisfactorily be extended to electrolytic reductions of the type considered in this paper. The activated stage in reduction is an electron transfer, governed by an interfacial potential barrier of the kind considered in the theory of hydrogen overvoltage (Gurney, *Proc. Roy. Soc.*, 1931, [*A*], **134**, 137). Efficiency in reduction implies that the electrons encounter less resistance due to the barrier between the cathode and the organic molecule than to that between the cathode and the solvent. A high hydrogen overvoltage, which implies a large cathode-solvent barrier, will permit the cathode to acquire a high negative potential, and will therefore facilitate the adsorption of the organic molecule by means of its reducible positive centres.

Experimental.

Preparation of Materials.—Sorbic acid, obtained in quantity by the condensation of malonic acid and freshly distilled crotonaldehyde in dry pyridine (Döbner, *Ber.*, 1900, **33**, 2140), had m. p. 134° (from petroleum, b. p. 80—100°).

Δ^{α}-*n*-Hexenoic acid made by Goldberg and Linstead's method (J., 1928, 2351) and recrystallised from petroleum (b. p. 40—60°) had m. p. 32·2°. The anilide prepared from the chloride had m. p. 110° (G. and L., *loc. cit.*, give 110°) (Found : C, 76·0; H, 8·0; N, 7·8. Calc. : C, 76·1; H, 8·0; N, 7·4%).

Δ^{β}-*n*-Hexenoic acid (cf. Linstead, Noble, and Boorman, J., 1933, 557) had b. p. 116—117°/18 mm. and m. p. 11°; these authors give m. p. 12°. The anilide had m. p. 55° (Found : C, 76·4; H, 8·0; N, 7·6. Calc. : C, 76·1; H, 8·0; N, 7·4%).

Δ^{γ}-*n*-Hexenoic acid, prepared in 20% yield by Letch and Linstead's method (J., 1934, 1994) from " hydrosorbic " acid obtained by the reduction of sorbic acid at a spongy copper cathode in alkaline solution (see expt. 9), had b. p. 109—110°/18 mm. and m. p. 1° (L. and L., *loc. cit.*, give m. p. 1°). The anilide had m. p. 87° (Found : C, 76·1; H, 8·1; N, 7·5. Calc. : C, 76·1; H, 8·0; N, 7·4%).

Reduction Technique.—Exploratory experiments were carried out in what we have called a differential apparatus (cf. Pomilio, *Z. Elektrochem.*, 1915, **21**, 444). Briefly, two similar electrolysis cells, embodying porous pots (7 × 2 cm. in diameter), were connected in series, the pots forming the cathode compartments. One cell served as a hydrogen coulombmeter, the other as a reduction cell. The hydrogen evolution from each unit was measured in two similar 5 c.c. gas burettes, immersed, up to their zero marks, in water. The reducing efficiency of any cathode in a given medium could, in this way, be rapidly determined with the use of a very small amount of material (0·1 g.). The current was 0·14 amp.

Reductions on a large scale (involving 10—20 g. of sorbic acid) were carried out in tall beakers (1000 c.c.); the cylindrical porous pots forming the anode compartments measured 16 × 4 cm.

in diameter and were conditioned before use as directed by Tafel (*Ber.*, 1900, **33**, 2216). Where possible, cylindrical cathodes (15 × 7 cm. in diameter) were used with strips of platinum foil as anodes, the anolyte was the same medium as the catholyte with the addition of a suitable salt (sodium acetate, sulphate, or carbonate) to prevent undue osmosis. A current of 1·0 amp. was used throughout and the temperature remained between 20° and 25° or was maintained within these limits by water-cooled glass spirals.

Preparation of Cathodes.—Mercury, purified by dilute nitric acid and distilled in a vacuum before use, formed, as a cathode, a layer (50 sq. cm.) a few mm. deep on the bottom of the beaker, the porous pot being suspended.

Cadmium (a commercial sample—Messrs. Harrington Bros., Ltd.) was fashioned into a cylinder and cleaned with dilute nitric acid. The reducing properties of the cathode were not influenced by electro-deposition of a spongy layer of cadmium.

Tin. A specimen of commercial sheet tin was used (Messrs. Johnson and Matthey and Co., Ltd.).

Lead. Two specimens were available: (a) a sample of assay lead (Messrs. Hopkin and Williams, Ltd.) which was shown by spectrographic analysis to contain the following impurities: Bi, 0·04—0·08; Cu, *ca.* 0·0002; Ag, 0·0005—0·001; Cd, 0·0002%; Tl, trace; and (b) a specimen of spectrographically pure lead (Messrs. Adam Hilger, Ltd.) which was guaranteed to contain less than 0·001% of impurity (probably Bi). The electrodes were alternately electrolytically oxidised and reduced in 2*N*-sulphuric acid and were preserved in the oxidised condition under distilled water (cf. Tafel, *loc. cit.*).

Copper, in the form of gauze (30 mesh), was first oxidised in air and then covered with a substantial deposit of copper by electrolysis of an acid solution of pure copper sulphate. The electrode was used immediately after washing.

Isolation and Purification of Reduction Products.—(a) *Reduction in aqueous acetic acid.* Acetic acid purified by Orton and Bradfield's method (J., 1927, 983), diluted to 70%, and made 0·5*M* with respect to sodium acetate, was employed as catholyte. On completion of a reduction the liquid (500—600 c.c.) was filtered, treated with 700 c.c. of concentrated hydrochloric acid, and cooled below 0°. In this way the major portion of any unreduced sorbic acid was removed (cf. Burton and Ingold, *loc. cit.*). The filtrate, diluted with water (500 c.c.), was repeatedly extracted with ether (12—15 times), the extract (3—4 l.) distilled through a long column, and the acetic acid removed by fractionation in a vacuum from a Claisen flask embodying a 12" Vigreux column. By cooling a solution of the residue in petroleum (b. p. 40—60°) to − 5°, more sorbic acid could be removed. The dihydro-acids were then distilled from a small fractionating Claisen flask at a rate not exceeding 2—5 drops/min. Under these conditions any residual sorbic acid remained in the flask (cf. Burton and Ingold, *loc. cit.*). The product was again distilled before analysis. In all these experiments the yield of pure reduction product was about 86% of the theoretical, the greater part of the loss occurring during the separation of the acetic acid. High-boiling " pinacol " product, formed only at a mercury cathode, was distilled under a fraction of a mm. without decomposition.

(b) *Reduction in* 2N-*sulphuric acid.* Only one reduction was attempted, because sorbic acid was only sparingly soluble in the aqueous acid. Reduction was finally complete, the product floating on the surface of the catholyte. After thorough extraction with ether, the extract was dried over sodium sulphate and treated as in (a) with the appropriate modifications. The yield of pure reduction product was 86% (expt. 2).

(c) *Reduction in neutral and in alkaline solutions.* For reduction in neutral solution the sorbic acid was dissolved in *N*/2-sodium bicarbonate, and the solution saturated with carbon dioxide throughout the reduction; in alkaline medium, sodium sorbate dissolved in *N*-sodium hydroxide was used. In both cases, after acidification with hydrochloric acid, the procedure was as in (a), the distillation with the object of separating acetic acid being of course omitted. The yield of purified reduction product was about 94% of the theoretical.

Analysis of Reduction Products.—(a) *Addition of bromine to the hexenoic acids.* In pure glacial acetic acid solution at room temperature, the reaction between bromine and pure Δ^{α}-*n*-hexenoic acid, in initial concentrations *N*/20 and *M*/80 respectively, was slow and occurred only to the extent of about 10% in 5 hours. In 50% aqueous acetic acid as solvent, addition was rapid and quantitatively complete in 4 hours; Δ^{β}- and Δ^{γ}-*n*-hexenoic acids reacted completely in less than 2 hours.

(b) *Addition of iodine to the hexenoic acids.* Δ^{α}-*n*-Hexenoic (*M*/80) in sodium bicarbonate solution reacted with iodine (*N*/20) at room temperature only to the extent of 1·1% in 8 hours

(cf. Linstead and May, J., 1927, 2565). During the same period of time the addition to Δ^{β}- and Δ^{γ}-*n*-hexenoic acids was quantitatively complete.

The analysis of the reduction product was carried out in narrow-mouthed glass-stoppered bottles (150 c.c.). The concentrations of halogen and unsaturated acid were $N/20$ and $M/80$ (had reaction occurred completely, there would thus have been 2 equivs. of halogen). Each estimation was performed in duplicate. After a suitable period of time, potassium iodide solution (10%) was added to the reaction mixture involving bromine, and concentrated hydrochloric acid to that involving sodium bicarbonate solution, the iodine liberated being titrated with $N/10$-thiosulphate.

The bromine absorbed therefore corresponds to the total dihydro-acids (Δ^{α}-, Δ^{β}-, and Δ^{γ}-*n*-hexenoic acids) present in the reduction product and is given as a percentage (B). The iodine absorption, which represents Δ^{β}- and Δ^{γ}-acids, is also given (J%). In the experiments recorded below, the substantial equality of these two figures with 100 establishes the absence of hexoic and Δ^{α}-*n*-hexenoic acids.

Ozonolysis. The method was essentially that of Burton and Ingold (*loc. cit.*). The reduction product (2—5 g.) was treated in chloroform solution at 0° with ozonised oxygen until the solution was saturated towards bromine. An artificial mixture of Δ^{β}- and Δ^{γ}-*n*-hexenoic acids (Δ^{γ}-, 50%) gave the following results: (1) 5·000 g. gave 2·300 g. of succinic acid (Found: Δ^{γ}-*n*-hexenoic acid, 44·5%); (2) 4·750 g. gave 2·170 g. of succinic acid (Found: Δ^{γ}-*n*-hexenoic acid, 44·1%); (3) 3·985 g. gave 1·822 g. of succinic acid (Found: Δ^{γ}-*n*-hexenoic acid, 44·2%). These figures give a mean factor for the conversion of Δ^{γ}-*n*-hexenoic acid into succinic acid of 88·5%, in good agreement with that (90%) found and used by the above authors.

Details of Typical Reductions.—Expt. 1. *Mercury in acetic acid.* The current efficiency was very high. Sorbic acid (20 g.) after the passage of 20 amp. hr. (theoretical for dihydro-acid, 10 amp. hr.) gave a product distilling in two fractions: (a) 6·8 g., b. p. 105—106°/14 mm. [Found: B, 99·4; J, 99·6; $\Delta^{\beta} + \Delta^{\gamma}$, 99·4; Δ^{γ} (by ozonolysis), 53·7, 54·9%]; (b) 10·2 g. of "pinacol," b. p. 180—182°/< 1 mm. [Found: C, 64·2; H, 8·0; M (Rast), 231; M (by titration as a dicarboxylic acid), 227. Calc. for $C_{10}H_{18}(CO_2H)_2$: C, 63·7; H, 8·0%; M, 226].

Expt. 2. *Mercury in sulphuric acid.* The reduction product from sorbic acid (20 g.) consisted of: (a) 6·4 g., a colourless liquid, b. p. 105—106°/14 mm. [Found: B, 99·5; J, 99·6; $\Delta^{\beta} + \Delta^{\gamma}$, 99·5; Δ^{γ} (by ozonolysis), 52·1%]; (b) 11·1 g. of "pinacol," b. p. 184—186°/< 1 mm. [Found: C, 64·2; H, 8·0; M (Rast), 231, 242; M (by titration as a dicarboxylic acid), 226·8].

Expt. 3. *Mercury in neutral solution.* Sorbic acid (20 g.) gave (a) a colourless liquid (15·0 g.), b. p. 103—104°/13 mm. [Found: B, 99·7; J, 99·6; $\Delta^{\beta} + \Delta^{\gamma}$, 99·6; Δ^{γ} (by ozonolysis), 40·9, 41·5, 41·1%], and (b) a light brown "pinacol" (4·1 g.), b. p. 180—183°/< 1 mm.

Expt. 4. *Mercury in alkaline solution.* Sorbic acid (18 g.) gave (a) 11·7 g., b. p. 103—104°/13 mm. [Found: B, 99·7; J, 99·5; $\Delta^{\beta} + \Delta^{\gamma}$, 99·5; Δ^{γ} (by ozonolysis), 39·3, 40·7%], and (b) 5·0 g. of "pinacol," b. p. 178—180°/< 1 mm.

Expt. 5 (*as* 4). Sorbic acid (40 g.) gave (a) a colourless liquid (27·3 g.), b. p. 100—101°/11 mm. (Found: B, 99·8; J, 99·9; $\Delta^{\beta} + \Delta^{\gamma}$, 99·8%), and (b) "pinacol" (10·7 g.), b. p. 178—181°/< 1 mm.

Expt. 6. *Cadmium in acetic acid.* The reduction was fairly efficient. Sorbic acid (10 g.) gave, after the passage of six times the theoretical (for dihydro-acid) amount of current, (a) unchanged sorbic acid (2·4 g.) and (b) 6·0 g., b. p. 108—109°/15—16 mm. [Found: B, 100·0; J, 99·7; $\Delta^{\beta} + \Delta^{\gamma}$, 99·7; Δ^{γ} (by ozonolysis), 54·0, 53·9%].

Expt. 7. *Cadmium in alkaline solution.* The reduction was more efficient than in expt. 6. Sorbic acid (20 g.) gave, after the passage of five times the theoretical (for dihydro-acid) amount of current, an acid, b. p. 100—101°/11 mm. (18·9 g.; 95%) [Found: B, 99·8; J, 99·8; $\Delta^{\beta} + \Delta^{\gamma}$, 99·8; Δ^{γ} (by ozonolysis), 38·4, 38·8%].

Expt. 8. *Copper in acetic acid.* The products from sorbic acid (12 g.) and six times the theoretical (for dihydro-acid) amount of current were: (a) unchanged sorbic acid (3·0 g.) and (b) a colourless liquid (8·0 g.), b. p. 102—103°/12 mm. [Found: B, 99·6; J, 99·3; $\Delta^{\beta} + \Delta^{\gamma}$, 99·3; Δ^{γ} (by ozonolysis), 50·0%].

Expt. 9. *Copper in alkaline solution.* Sorbic acid (20 g.) gave a 96% yield of a liquid, b. p. 102—103°/12 mm. (18·5 g.) [Found: B, 99·6; J, 99·7; $\Delta^{\beta} + \Delta^{\gamma}$, 99·6; Δ^{γ} (by ozonolysis), 39·8, 39·4%]. The current efficiency was very high.

Reduction of Anthracene.—Anthracene, dissolved in moist ethyl alcohol or, better, in dioxan, was easily reduced by magnesium or aluminium amalgam to 9 : 10-dihydroanthracene, identified by m. p. and mixed m. p. with an authentic specimen. The reduction of anthracene in ethyl-

alcoholic solution by sodium amalgam has been already described (Graebe and Liebermann, *Annalen*, Suppl., 1870, **7**, 265).

Anthracene (0·1 g.) in ethyl alcohol (40 c.c., 95%) containing ammonium sulphate (0·2 g.) and aqueous ammonia (0·5 c.c.) was reduced to the dihydro-compound at a mercury cathode. No reduction occurred when the solution was acidified with sulphuric acid containing sodium sulphate. Reduction at a mercury cathode was also found to be possible in aqueous-alcoholic sodium hydroxide and tetramethylammonium hydroxide (the latter was prepared by shaking the pure chloride with silver oxide).

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45. *Observations upon the Mechanism of Permanganate Reduction and the Induced Oxidation of Chlorion.*

By Henry Bassett and Isabella Sanderson.

The use of internal indicators in dichromate titrations (Knop, *J. Amer. Chem. Soc.*, 1924, **46**, 263) has removed most of the practical interest attached to the titration of ferrous chloride solutions by permanganate, but observations made in a study of the titration throw some light on the mechanism of oxidation by permanganate.

The excess consumption of permanganate in the titration of ferrous salts in presence of chloride was first noticed by Löwenthal and Lenssen (*Z. anal. Chem.*, 1862, **1**, 329). It is generally small, but has led to much investigation and speculation (Zimmermann, *Ber.*, 1881, **14**, 779; *Annalen*, 1882, **213**, 307; Wagner, *Z. physikal. Chem.*, 1889, **28**, 33; Manchot, *Annalen*, 1902, **325**, 93; Manchot and Wilhelms, *ibid.*, p. 105; Skrabal, *Z. anal. Chem.*, 1903, **42**, 359; Friend, J., 1909, **95**, 1228; Kolthoff and Smit, *Pharm. Weekblad*, 1924, **61**, 1082). Addition of manganese sulphate decreases the error; this device was first proposed by Kessler (*Pogg. Ann.*, 1863, **118**, 48; **119**, 225; *Z. anal. Chem.*, 1882, **21**, 381) and revived by Zimmermann (*loc. cit.*). Opinion differs as to the amount to be added (Treadwell, " Analytical Chemistry," 1905, Vol. II, 483; Harrison and Perkin, *Analyst*, 1908, **33**, 43; Friend, *loc. cit.*).

Liberation of small amounts of chlorine, induced in some way by the other reaction, is the cause of the phenomenon. This was at first attributed to a " peroxide " formed from the ferric salt (Zimmermann; Manchot; Skrabal; *locc. cit.*) or to a hydroferrochloric acid (*e.g.*, $HFeCl_3$), which was supposed to be oxidised more readily than chlorion to chlorine (Wagner, *loc. cit.*).

Such explanations are inadequate since, in the oxidation of oxalic acid by permanganate in presence of hydrochloric acid, excess of permanganate is always required, and manganese sulphate is as effective in diminishing the excess in this case as in the foregoing (Gooch and Peters, *Z. anorg. Chem.*, 1899, **21**, 185; Skrabal, *ibid.*, 1904, **42**, 1). In our opinion, the liberation of chlorine is due to tervalent manganese which probably plays as important a part in all reactions involving acid permanganate as Skrabal (*loc. cit.*, 1904) and Launer (*J. Amer. Chem. Soc.*, 1932, **54**, 2597) showed it to do in the reaction with oxalic acid.

Although compounds of tervalent manganese are very unstable, a few have been prepared in the solid state (Kehrmann, *Ber.*, 1887, **20**, 1594; Christensen, *Dansk Vid. Selsk. Förh.*, 1896, 94; *J. pr. Chem.*, 1887, **35**, 57; Fichter and Brunner, J., 1928, 1862; Mellor, " Comprehensive Treatise, etc.," 1932, Vol. XII, 460). They have a cherry-red colour either as solids or in solution, whereas salts of quadrivalent manganese are yellow or brown (Weinland and Lauenstein, *Z. anorg. Chem.*, 1899, **20**, 40; Fichter and Brunner, *loc. cit.*). We find that a cherry-red colour is produced when permanganate is added to solutions of manganese sulphate strongly acidified with sulphuric acid. This colour persists for several days in the absence of oxidisable material, but the solution gradually gets paler and deposits manganese dioxide.

The explanation appears to be that tervalent manganese, formed by the reaction $MnO_4' + 4Mn^{\cdot\cdot} + 8H^{\cdot} \longrightarrow 5Mn^{\cdot\cdot\cdot} + 4H_2O$, is converted into relatively stable mangani-sulphate complexes which, however, slowly undergo the change $2Mn^{\cdot\cdot\cdot} \rightleftharpoons Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$. In presence of zinc hydroxide to maintain neutrality and prevent adsorption of $Mn^{\cdot\cdot}$ by the precipitate, the reaction $2MnO_4' + 3Mn^{\cdot\cdot} + 2H_2O = 5MnO_2 + 4H^{\cdot}$ goes to completion and is used for estimating manganese (Volhard, *Annalen*, 1879, **198**, 218). On the above basis, at least two steps are involved :

$$\begin{cases} 2MnO_4' + 8Mn^{\cdot\cdot} + 16H^{\cdot} \longrightarrow 10Mn^{\cdot\cdot\cdot} + 8H_2O \\ 10Mn^{\cdot\cdot\cdot} + 10H_2O \longrightarrow 5Mn^{\cdot\cdot} + 5MnO_2 + 20H^{\cdot} \end{cases}$$

The cherry-red colour can also be noticed in an ordinary titration of ferrous sulphate in presence of sulphuric acid. If the permanganate is added, drop by drop, while the ferrous solution is rotated in the flask, the purple colour is seen to give rise to quite a distinct red colour which is quickly bleached. As this red colour can be seen from the beginning of the titration, it appears that $Mn^{\cdot\cdot\cdot}$ is the first identifiable stage in the acid reduction of permanganate and probably precedes the complete reduction to $Mn^{\cdot\cdot}$ in all cases. There is no indication that a yellowish stage due to quadrivalent manganese intervenes between the purple and the cherry-red stage.

Manganese sulphate solutions strongly acidified with phosphoric acid show the same colour changes as do sulphuric acid solutions on treatment with permanganate. The precipitate slowly formed as the cherry-red solutions gradually lose their colour is not manganese dioxide, however. It is of a greenish-buff colour and of somewhat variable composition. A typical sample, washed with dilute phosphoric acid, then with acetone, and air-dried, gave on analysis: Available oxygen, 4·06; P_2O_5, 41·73; MnO, 35·97; loss on ignition, 22·22%. Consideration of various possibilities suggests that the material is a mixture of manganous salts of complex quadrivalent-manganese-phosphoric acids. Mixtures of $[Mn^{II}(H_2O)_4]^{\cdot\cdot}[Mn^{IV}(PO_4)_2]''$, $[Mn^{II}(H_2O)_4]^{\cdot\cdot}{}_2[Mn^{IV}(HPO_4)_4]''''$, and MnO_2 in suitable proportions would account for the analytical figures.

Christensen (*Dansk Vid. Selsk. Skr.*, 1883, **2**, 148, 151), by a somewhat similar method at 100°, obtained a product of the same character as ours, to which, however, he attributed the formula $MnPO_4,H_2O$, with only tervalent manganese. Although the product is of rather variable composition, the evidence appears to favour our view of its nature rather than Christensen's.

The insolubility of this substance in strongly acid solutions led us to try whether phosphoric acid could be removed from acid solution by means of manganese and nitric acid, as it can be by tin and nitric acid (Reynoso, *Compt. rend.*, 1851, **33**, 385; *J. pr. Chem.*, 1851, **54**, 261). This is indeed the case, and either metallic manganese or a soluble manganese salt may be used. A mixture of 0·5 g. of manganese (metal), 0·4 g. of diammonium hydrogen phosphate, 10 c.c. of concentrated nitric acid, and 10 c.c. of water was heated to about 70° for 12 hours; a dark buff-coloured precipitate formed, which was filtered off and washed with dilute nitric acid, and the filtrate contained no phosphate. In another experiment, 2·5 g. of manganese chloride tetrahydrate were used in place of the metallic manganese, but otherwise the procedure was the same; in this case the filtrate contained 0·0031 g. of P_2O_5.

Analysis showed the buff precipitate to be essentially similar in character to that obtained by decomposition of the cherry-red manganic phosphate solutions. A typical sample contained: Available oxygen, 4·91; P_2O_5, 41·86; MnO, 39·38; loss on ignition, 18·96%.

When permanganate is added to solutions containing oxalic acid and manganese sulphate, a cherry-red colour is obtained which gradually or rapidly (according to the concentrations, etc.) becomes brownish-yellow. Addition of alkali oxalate or acetate causes the cherry-red colour to return. The observations set out above make it likely that the colour change from red to yellow is due to the change $2Mn^{\cdot\cdot\cdot} \rightleftharpoons Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$. Both the $Mn^{\cdot\cdot\cdot}$ and the $Mn^{\cdot\cdot\cdot\cdot}$ ions would be mainly in the form of complex oxalate anions. Decomposition on the above lines of the $Mn^{\cdot\cdot\cdot}$ complex might well involve liberation of oxalate ions. This

would explain why addition of these restores the red colour. Acetate ions would act in the same way owing to formation of acetate complexes. Skrabal (*loc. cit.*) considered that he had some kinetic evidence for the above change. The kinetics of the oxalate reaction have recently been re-examined by Lidwell and Bell (J., 1935, 1303).

Now ter- and quadri-valent manganese are more potent oxidising agents than permanganate under comparable conditions. The normal potential for the reduction $MnO_4' + 8H^{\cdot} + 5e \rightleftharpoons Mn^{\cdot\cdot} + 4H_2O$ is + 1·761 volts on the absolute zero scale (normal calomel electrode = 0·56 volt), while that for reduction only to $Mn^{\cdot\cdot\cdot}$ would be + 1·755 volts. The normal potentials for the reactions $Mn^{\cdot\cdot\cdot\cdot} + 2e \rightleftharpoons Mn^{\cdot\cdot}$ and $Mn^{\cdot\cdot\cdot} + e \rightleftharpoons Mn^{\cdot\cdot}$ are said to be + 1·854 and + 1·788 volts respectively on the same scale (see Grube and Huberich, *Z. Elektrochem.*, 1923, **29**, 8, and "International Critical Tables," 1929, vol. VI, 333, where the potentials are given with reference to the normal hydrogen electrode). Since the normal potential of $MnO_4' \longrightarrow Mn^{\cdot\cdot\cdot}$ is little less than that of $Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$, it is evident that relatively small changes in concentration (*e.g.*, of $Mn^{\cdot\cdot}$) would enable the latter to be oxidised to $Mn^{\cdot\cdot\cdot}$ by permanganate. Any process converting $Mn^{\cdot\cdot\cdot}$ into a complex would be particularly favourable. Since there is not enough difference between the normal potentials of $MnO_4' \longrightarrow Mn^{\cdot\cdot\cdot}$ and of $Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$ to explain why $Mn^{\cdot\cdot\cdot}$ can apparently oxidise chloride ion so much more rapidly than can MnO_4', some other explanation for this is necessary. It may well depend upon the much greater simplicity of the change $Mn^{\cdot\cdot\cdot} + Cl' \longrightarrow Mn^{\cdot\cdot} + Cl$ than of $MnO_4' + 4Cl' + 8H^{\cdot} \longrightarrow Mn^{\cdot\cdot\cdot} + 2Cl_2 + 4H_2O$.*

Any factor which increases the stability of $Mn^{\cdot\cdot\cdot}$ will also lower its oxidation potential and its capacity for liberating chlorine. Ions able to form complex ions with $Mn^{\cdot\cdot\cdot}$ should have this effect. The stability of $Mn^{\cdot\cdot\cdot}$ would also be increased, aud its oxidatiou potential reduced, by addition of $Mn^{\cdot\cdot}$. This effect is allowed for in the usual expression for the potential of an electrode at which the reaction $Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$ is proceeding reversibly (*viz.*, $1{\cdot}788 + 0{\cdot}058 \log [Mn^{\cdot\cdot\cdot}]/[Mn^{\cdot\cdot}]$ volts at 17°, 1·788 being the normal potential). Although the normal potential for $\frac{1}{2}Cl_2 \longrightarrow Cl'$ (Cl_2 at 1 atm.) is + 1·635 volts, yet that for $Fe^{\cdot\cdot\cdot} \longrightarrow Fe^{\cdot\cdot}$ is only + 1·025 volts, so that ferrous iron is readily and rapidly oxidised by any of the possible stages in the reduction of MnO_4' to $Mn^{\cdot\cdot}$.

Normal potentials can only be used as qualitative guides as to what may happen in permanganate titrations, since the actual oxidation potentials will depend upon various concentrations which are usually unknown.

A series of titrations summarised in the tables showed that the excess consumption of permanganate in ferrous chloride–permanganate titrations could, in fact, be substantially eliminated by addition of considerable amounts of sulphuric, phosphoric, or hydrofluoric acids, and even, somewhat paradoxically, of hydrochloric acid, all of which give rise to complex manganic anions. Lithium chloride was found to be effective (last table), and the effect of manganous salts is shown in the two preceding tables.

Titrations by permanganate of ferrous chloride solutions containing small amounts of extra hydrochloric acid are most accurate when the solutions are made 2—3N with regard to sulphuric acid. No manganese sulphate need be added. The concentration of the iron should be between 0·05 and 0·1N. The end-point is then sharp and lasts for some minutes. The instability of the end-point is a serious difficulty in all titrations of ferrous chloride solutions with permanganate. By the methods indicated above, the rate of oxidation of chlorion can be repressed so much, relatively to that of the ferrous ion, that a very close approximation to the correct end-point is obtainable, but when all ferrous iron is removed, slow oxidation of chlorion continues, with the result that the pink end-point colour fades whether it be due to MnO_4' or to $Mn^{\cdot\cdot\cdot}$ ions. Increased acidity caused by acid addition should have little, if any, effect on the fading, for although the rate of the reduction stage $MnO_4' \longrightarrow Mn^{\cdot\cdot\cdot}$ depends on the eighth power of the hydrogen-ion concentration, that of the $Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$ stage is independent of it.

* This point has been considered by Ubbelohde (J., 1935, 1605), though he does not attribute loss of chlorine in permanganate titrations to the $Mn^{\cdot\cdot\cdot}$ ion, as we do. He recommends the use of a manganic sulphate solution instead of permanganate for the titration of ferrous iron in presence of chloride, but the concentration of sulphuric acid in this solution is such as gave good results with permanganate in the present investigation.

It appears likely that the rapidity of the fading is mainly due to the change $2Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$ (possibly accelerated by hydrogen ions). The normal potential of $Mn^{\cdot\cdot\cdot\cdot}$ being so high (+ 1·854 volts), its capacity to liberate chlorine would be much less checked by the methods which were reasonably effective for $Mn^{\cdot\cdot\cdot}$. The $Mn^{\cdot\cdot\cdot\cdot}$ ion, formed from $Mn^{\cdot\cdot\cdot}$, could hardly appear so long as any ferrous iron remained unoxidised, and it is unlikely that it plays any part in an ordinary permanganate titration of ferrous iron although it may well do so in the slower oxalate reaction.

With high chlorion concentration, the end-point is also obscured by formation of reddish-brown $[FeCl_4]'$ ions. This can be prevented by addition of phosphoric acid, which forms much more stable but nearly colourless ferriphosphoric anions (Reinhardt, *Chem.-Ztg.*, 1889, **13**, 323).

Experimental.

The ferrous chloride solution was made by dissolving pure iron wire in hydrochloric acid, an excess of the latter being used which ranged from about 10 to 20 c.c. of $4N$-acid per litre of ferrous chloride solution. The solutions were standardised by means of potassium dichromate,

(I) $FeCl_2$–HCl–$KMnO_4$ Series.

(*a*) $KMnO_4 = 0·1322N$; $FeCl_2 = 0·1520N$; 20 c.c. $FeCl_2$ = 22·99 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. (water)	23·41	0·42	>3 mins.
20 ,, 1·8*N*-HCl	23·20	0·21	2½ ,,
20 ,, 1·8 ,,	23·24	0·25	2½ ,,
20 ,, 2·9 ,,	23·19	0·20	1½ ,,
20 ,, 2·9 ,,	23·18	0·19	1½ ,,
20 ,, 3·5 ,,	23·16	0·17	40 secs.
20 ,, 4·8 ,,	23·10	0·11	20 ,,
20 ,, 4·8 ,,	23·10	0·11	20 ,,
20 ,, 5·4 ,,	23·20	0·21	15 ,,

(*b*) $KMnO_4 = 0·09755N$; $FeCl_2 = 0·09375N$; 20 c.c. $FeCl_2$ = 19·22 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. 0·59*N*-HCl	19·50	0·28	7 mins.
20 ,, 0·59 ,,	19·48	0·26	
20 ,, 0·71 ,,	19·48	0·26	
20 ,, 1·8 ,,	19·38	0·16	3 mins.
20 ,, 2·5 ,,	19·32	0·10	*ca.* 3 ,,
20 ,, 2·7 ,,	19·32	0·10	2 ,,
20 ,, 2·7 ,,	19·33	0·11	2 ,,
20 ,, 3·6 ,,	19·25	0·03	*ca.* 1½ ,,

(II) $FeCl_2$–H_2SO_4–$KMnO_4$ Series.

(*a*) $KMnO_4 = 0·1332N$; $FeCl_2 = 0·1514N$; 20 c.c. $FeCl_2$ = 22·91 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. (water)	23·25	0·34	
20 ,, 0·62*N*-H_2SO_4	23·12	0·21	
20 ,, 0·62 ,,	23·10	0·19	
20 ,, 1·3 ,,	23·08	0·17	*ca.* 2 mins.
20 ,, 1·3 ,,	23·03	0·12	
20 ,, 3·4 ,,	23·02	0·11	
20 ,, 6·0 ,,	23·02	0·11	*ca.* 2 mins.

(*b*) $KMnO_4 = 0·09725N$; $FeCl_2 = 0·05825N$; 20 c.c. $FeCl_2$ = 11·97 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. (water)	12·15	0·18	
20 ,, 0·62*N*-H_2SO_4	12·08	0·11	
20 ,, 1·3 ,,	12·01	0·04	
20 ,, 1·3 ,,	11·98	0·01	
20 ,, 3·4 ,,	12·00	0·03	
20 ,, 4·7 ,,	12·01	0·04	
20 ,, 4·7 ,,	12·02	0·05	
20 ,, 6·0 ,,	11·99	0·02	*ca.* 12 mins.

(III) $FeCl_2$–H_3PO_4–$KMnO_4$ Series.

(*a*) $KMnO_4 = 0·1332N$; $FeCl_2 = 0·1680N$; 20 c.c. $FeCl_2$ = 25·23 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. (water)	25·78	0·55	
20 ,, 1·1*N*-H_3PO_4	25·50	0·27	40 secs.
20 ,, 2·1 ,,	25·33	0·10	20 ,,
20 ,, 3·1 ,,	25·27	0·04	16 ,,
20 ,, 3·1 ,,	25·30	0·07	16 ,,
20 ,, 5·2 ,,	25·25	0·02	*ca.* 5 ,,
20 ,, 5·2 ,,	25·25	0·02	*ca.* 5 ,,

(*b*) $KMnO_4 = 0·09725N$; $FeCl_2 = 0·05286N$; 20 c.c. $FeCl_2$ = 11·90 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. 1·1*N*-H_3PO_4	11·99	0·09	*ca.* 2½ mins.
20 ,, 2·1 ,,	12·00	0·10	
20 ,, 2·6 ,,	11·94	0·04	
20 ,, 2·6 ,,	11·97	0·07	
20 ,, 3·1 ,,	11·95	0·05	30 secs.
20 ,, 3·1 ,,	11·97	0·07	30 ,,
20 ,, 5·2 ,,	11·91	0·01	*ca.* 7 ,,
20 ,, 5·2 ,,	11·90	0·00	

(IV) $FeCl_2$–HF–$KMnO_4$ Series.

(*a*) $KMnO_4 = 0·1641N$; $FeCl_2 = 0·1914N$; 20 c.c. $FeCl_2$ = 23·34 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. 0·3*N*-HF	23·66	0·32	*ca.* 3 mins.
20 ,, 0·3 ,,	23·65	0·31	*ca.* 3 ,,
20 ,, 0·6 ,,	23·64	0·30	2—3 mins.
20 ,, 0·6 ,,	23·60	0·26	
20 ,, 2·1 ,,	23·41	0·07	*ca.* 7 secs.
20 ,, 2·1 ,,	23·41	0·07	*ca.* 7 ,,

(*b*) $KMnO_4 = 0·07565N$; $FeCl_2 = 0·05946$; 20 c.c. $FeCl_2$ = 15·72 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. 0·20*N*-HF	16·04	0·32	colour slightly faded after 3 mins. (both rows)
20 ,, 0·20 ,,	16·00	0·28	
20 ,, 0·60 ,,	15·92	0·20	30 secs.
20 ,, 0·60 ,,	15·94	0·22	30 ,,
20 ,, 2·1 ,,	15·85	0·13	5 ,,
20 ,, 2·1 ,,	15·88	0·16	

(V) $FeCl_2$–$MnSO_4$–$KMnO_4$ Series.

1 C.c. of Mn solution = 0·60 g. $MnSO_4,4H_2O$. 20 C.c. 0·7*N*-HCl were added to the 20 c.c. of $FeCl_2$ solution. $KMnO_4$ = 0·1332*N*; $FeCl_2$ = 0·1711*N*; 20 c.c. $FeCl_2$ = 25·54 c.c. $KMnO_4$ (calc.).

Mn soltn. added, c.c.	H_2O added, c.c.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
—	10	26·10	0·56	
1	9	25·82	0·28	Pink colour not bleached after 5 mins.
1	9	25·81	0·27	(Pink colour not bleached after 5 mins.)
2	8	25·71	0·17	2 mins.
2	8	25·72	0·18	2 ,,

Mn soltn. added, c.c.	H_2O added, c.c.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
3	7	25·71	0·17	$1\frac{1}{2}$ mins.
3	7	25·70	0·16	$1\frac{1}{6}$,,
5	5	25·71	0·17	45 secs.
7	3	25·70	0·16	20 ,,
10	—	25·71	0·17	3 ,,

(VI) $FeCl_2$–$MnCl_2$–$KMnO_4$ Series.

1 C.c. of Mn solution = 0·6 g. $MnCl_2,4H_2O$. 20 C.c. 0·7*N*-HCl were added to the 20 c.c. of $FeCl_2$ solution. $KMnO_4$ = 0·1332*N*; $FeCl_2$ = 0·1680*N*; 20 c.c. $FeCl_2$ = 25·23 c.c. $KMnO_4$ (calc.).

Mn soltn. added, c.c.	H_2O added, c.c.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
—	10	25·65	0·42	
1	9	25·52	0·29	2 mins.
2	8	25·46	0·23	30 secs.
4	6	25·44	0·21	20 secs.
5	5	25·45	0·22	20 ,,
7	3	25·45	0·22	7 ,,

(VII) $FeCl_2$–LiCl–$KMnO_4$ Series.

1 C.c. of solution = 0·55 g. LiCl. 20 C.c. of 0·23*N*-HCl were added to the 20 c.c. of $FeCl_2$ solution. $KMnO_4$ = 0·05609*N*; $FeCl_2$ = 0·07655*N*; 20 c.c. $FeCl_2$ = 27·34 c.c. $KMnO_4$ (calc.).

LiCl soltn. added, c.c.	H_2O added, c.c.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
—	20	27·82	0·48	
10	10	27·41	0·07	20 secs.
10	10	27·44	0·10	20 secs.
20	—	27·33	0	

diphenylamine being used as internal indicator. The calculated permanganate values in the tables are based on the dichromate titrations. 20 C.c. of the ferrous chloride solution were used in each experiment; other additions are shown in the tables. Permanganate was run in slowly and, towards the end of the titration, drop by drop. The duration of the end-point colour was determined by means of a stop-clock. The experiments with hydrofluoric acid were carried out in wax beakers.

SUMMARY.

1. In the interaction of ferrous iron and permanganate, the first identifiable product of reduction of the latter is manganic ion, $Mn^{\cdots}$. This may also be formed by direct oxidation of $Mn^{\cdot\cdot}$ by permanganate.

2. The quadrivalent $Mn^{\cdots\cdot}$ ion may be formed from $Mn^{\cdots}$ by the change $2Mn^{\cdots} \rightleftharpoons Mn^{\cdot\cdot} + Mn^{\cdots\cdot}$; but indications appear to be against its being a direct and intermediate product of reduction of permanganate in acid solution.

3. Ter- and quadri-valent manganese are more potent oxidising agents than permanganate under comparable conditions, and the induced oxidation of chlorion in permanganate reactions is attributed to them, especially to the former. This may be partly because *reduction of* $Mn^{\cdots}$ *to* $Mn^{\cdot\cdot}$ *is a simpler process than reduction of* MnO_4' *to* $Mn^{\cdots}$.

4. A more correct end-point in the titration of ferrous chloride solutions by permanganate can be obtained by increasing the stability of $Mn^{\cdots}$ ions and thus lowering their oxidation potential. This can be done by addition either of manganous ions or of anions which can form stable complexes with $Mn^{\cdots}$, such as sulphate, phosphate, fluoride, or even chloride.

5. The end-point colour is always very unstable. It is considered that this is mainly due to the change $2Mn^{\cdots} \rightleftharpoons Mn^{\cdot\cdot} + Mn^{\cdots\cdot}$ and production of $Mn^{\cdots\cdot}$ ions with a much higher oxidation potential.

6. The most satisfactory titrations of ferrous chloride solutions with permanganate are obtained after making them 2—3*N* with respect to sulphuric acid.

7. Phosphate can be practically completely removed from solutions by digestion with concentrated nitric acid and manganese metal or salts. An insoluble product is formed which appears to be a manganous salt of a quadrivalent-manganese-phosphoric acid.

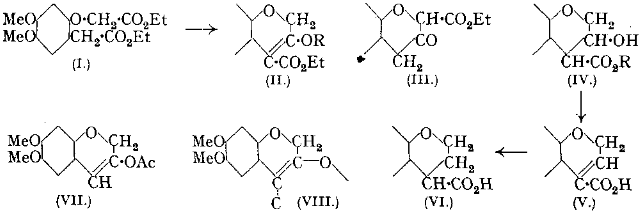
THE UNIVERSITY OF READING. [*Received, November 29th*, 1935.]

46. *Experiments on the Synthesis of Rotenone and its Derivatives. Part VIII. Netoric Acid and Toxicaric Acid.*

By Alexander Robertson and George L. Rusby.

By the fission of tetrahydrorotenol (dihydrorotenolic acid of older nomenclature) with alkaline hydrogen peroxide, Smith and La Forge (*J. Amer. Chem. Soc.*, 1930, **52**, 4595) obtained a monocarboxylic acid, netoric acid, $C_{12}H_{14}O_5$, m. p. 91—92°, which separated from water as a hydrate (compare Clark, *ibid.*, 1932, **54**, 2537). Subsequently the same compound was prepared from rotenol by Takei and his co-workers (*Ber.*, 1932, **65**, 279) and by Butenandt and McCartney (*Annalen*, 1932, **494**, 17). The former authors considered that the acid formed a hydrate, m. p. 90°, from which they obtained anhydrous material (analysed), m. p. 131—132°, whereas the latter stated that it existed in two interconvertible modifications, m. p. 87 and 131°, giving analytical figures for both forms which are consistent with those of the anhydrous compound.

The application of the same method of degradation to *apo*toxicarol by Clark (*loc. cit.*) and to toxicarol and rotenone by Butenandt and Hilgetag (*Annalen*, 1932, **495**, 172; 1933, **506**, 158) gave an unsaturated acid, toxicaric (dehydronetoric) acid, $C_{12}H_{12}O_5$, which on catalytic reduction readily yielded netoric acid. Under favourable conditions there was simultaneously formed from *apo*toxicarol a hydroxynetoric acid capable of being dehydrated to toxicaric acid. These authors assigned structures (IV, R = H) and (V) to hydroxynetoric and toxicaric acids in accordance with the formula (VI) first proposed for netoric acid by La Forge and his collaborators (*J. Amer. Chem. Soc.*, 1931, **53**, 4400). These structures, which embody the chroman skeleton present in rotenone and toxicarol, have now been independently confirmed by synthetical experiments.



Cyclisation of *ethyl derrate* (I) by means of sodium in warm toluene gave the *ester* (II, R = H), which, since it is a homogeneous crystalline compound instantaneously soluble in dilute aqueous sodium hydroxide, giving a ferric chloride reaction, and readily forming an *acetate*, is obtained in the enolic form. Although this reaction might conceivably have taken an alternative route resulting in the formation of (III), the recognised activity of the methylene group in esters of phenylacetic acids clearly indicates the production of (II, R = H). Further, no trace of a second product could be obtained, a result in agreement with the ring closure of analogous esters recently carried out in these laboratories (unpublished results). Moreover, the subsequent conversion of the enol-ester into netoric acid and toxicaric acid is in keeping with the structure (II, R = H), since, quite apart from the analytical evidence, the synthesis of tetrahydrodehydrorotenone (Robertson, J., **1933**, 1163) proves, *inter alia*, the presence of the skeleton (VIII) in rotenone, and under the conditions employed in the degradation this skeleton would not be expected to yield a netoric acid derived from (III).

On reduction in alcohol with hydrogen at atmospheric pressure and a platinum catalyst the enol (II, R = H) yielded the *hydroxy-ester* (IV, R = Et), which on dehydration and subsequent hydrolysis of the crude product gave rise to 6 : 7-dimethoxy-Δ^3-chromene-4-carboxylic acid (V), identical in every way with a specimen of toxicaric acid obtained from

toxicarol according to the directions of Butenandt and Hilgetag (*loc. cit.*). This acid was also obtained directly from (IV, R = Et) by alkaline hydrolysis in less favourable yield.

Reduction of the acetate (II, R = Ac) according to the procedure of Roll and Adams (*J. Amer. Chem. Soc.*, 1931, **53**, 3469), followed by hydrolysis of the product, gave rise directly to netoric acid (VI) identical with a natural specimen. This acid (natural and synthetic) has been found to separate from water as the monohydrate, m. p. 90°, which readily loses water of crystallisation and gives the anhydrous form, m. p. 132—133°.

Efforts to convert the ester (II, R = H) into the 6 : 7-dimethoxychroman-3-one by hydrolysis under a number of conditions were unsuccessful, but it was ultimately found that derric acid, on being boiled with sodium acetate and acetic anhydride, gave a product which appears to be the *acetate* (VII) of the enolic form of this chromanone and on deacetylation yielded a solid exhibiting ketonic properties.

EXPERIMENTAL.

Ethyl 3-*Hydroxy*-6 : 7-*dimethoxy*-Δ^3-*chromene*-4-*carboxylate* (II, R = H).—On being boiled with alcohol (100 c.c.) and concentrated sulphuric acid (5 c.c.) for 12 hours, derric acid (10 g.) (Robertson, J., 1932, 1387) gave the *ester* (10 g.), which crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 64°, readily soluble in alcohol or acetone and almost insoluble in water (Found : C, 59·1 ; H, 6·7. $C_{16}H_{22}O_7$ requires C, 58·9 ; H, 6·7%).

A solution of this ester (5 g.) in toluene (45 c.c.) containing powdered sodium (0·6 g.) was heated on the steam-bath for 2 hours ; the fairly vigorous reaction which started after 10 minutes appeared to be almost complete after ½ hour. The cooled reaction mixture was extracted with three portions of 2% aqueous sodium hydroxide (100, 50, 50 c.c.), the combined extracts were acidified with hydrochloric acid, and 4 hours later the crude *enol-ester* was collected, washed, and dried. The compound was separated from dark-coloured impurities by means of boiling light petroleum (b. p. 60—80°) (charcoal) and then crystallised from the same solvent, forming colourless prisms (2 g.), m. p. 109—110° (Found : C, 60·0 ; H, 5·7. $C_{14}H_{16}O_6$ requires C, 60·0 ; H, 5·7%). It is sparingly soluble in cold alcohol, readily soluble in ethyl acetate, benzene, and aqueous sodium hydroxide, and with alcoholic ferric chloride gives a deep blue coloration, destroyed by water and becoming green on standing.

Evaporation of the toluene residues left only traces of unchanged ester.

Acetylation of the compound (1 g.) with acetic anhydride (10 c.c.) and pyridine (5 c.c.) on the steam-bath for ½ hour and then at room temperature for 48 hours gave rise to *ethyl* 6 : 7-*dimethoxy*-3-*acetoxy*-Δ^3-*chromene*-4-*carboxylate* (II, R = Ac), which separated from light petroleum (b. p. 40—60°) in colourless slender needles or diamond-shaped plates, m. p. 84°, readily soluble in alcohol, acetic acid, or benzene (ferric chloride reaction negative) (Found : C, 59·3 ; H, 5·7. $C_{16}H_{18}O_7$ requires C, 59·6 ; H, 5·6%).

Ethyl 3-*Hydroxy*-6 : 7-*dimethoxychroman*-4-*carboxylate* (*Ethyl Hydroxynetorate*) (IV, R = Et).—The ester (II, R = H) (1 g.) was hydrogenated in alcohol (500 c.c.) by means of hydrogen at atmospheric pressure and room temperature with the aid of a platinum oxide catalyst (Voorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1402) (0·1 g.) in the course of 3 hours (90 c.c. absorbed). Removal of the catalyst and solvent left the *hydroxy-ester* as an oily residue, which gradually solidified and then separated from benzene–light petroleum (b. p. 60—80°) in tufts of colourless slender needles, m. p. 106°, sparingly soluble in ether and readily soluble in benzene or alcohol (Found : C, 59·7 ; H, 6·2. $C_{14}H_{18}O_6$ requires C, 59·6 ; H, 6·4%). The ferric chloride reaction was negative.

The reduction did not proceed when ethyl acetate was used as the solvent.

6 : 7-*Dimethoxy*-Δ^3-*chromene*-4-*carboxylic Acid* (*Toxicaric Acid*) (V).—A solution of the aforementioned hydroxy-ester (0·8 g.) in acetic anhydride (4 c.c.) was refluxed for 1·5 minutes, the anhydride decomposed with water (150 c.c.), the aqueous liquor extracted several times with ether, and the combined extracts washed with aqueous sodium bicarbonate. The pale brown oil left on evaporation of the ether was heated on the steam-bath with alcohol (15 c.c.) and water (3 c.c.) containing potassium hydroxide (0·6 g.) for 1 hour and diluted with water (10 c.c.), the greater part of the alcohol was evaporated, and the cooled residue acidified (Congo-red) with hydrochloric acid. Several hours later the brown acid was collected, washed, and crystallised from aqueous acetone (charcoal), forming pale yellow, short, thick or rod-like prisms with square ends, m. p. 210—211° (decomp.), having the properties of natural toxicaric acid (Found : C, 61·2 ; H, 5·3. Calc. for $C_{12}H_{12}O_5$: C, 61·0 ; H, 5·1%). Mixed with an

authentic specimen, it showed no depression in the m. p. (Butenandt and Hilgetag, *loc. cit.*, and Clark, *loc. cit.*, give m. p. 210° and 212° respectively).

Hydrolysis of the crude reduction product of the enol-ester (0·5 g.) under the same conditions gave rise to toxicaric acid (0·15 g.), m. p. and mixed m. p. 210—211° (decomp.) after crystallisation from acetone–light petroleum and then aqueous acetone.

In the course of the preparation of toxicaric acid from toxicarol by Butenandt and Hilgetag's method (*loc. cit.*) evaporation of the aqueous-acetone liquors left after crystallisation of the crude toxicaric acid deposited a product, m. p. about 188°, which, when examined under the microscope, appeared to be a mixture of toxicaric acid and hydroxynetoric acid. Treatment of this material with acetic anhydride according to Clark's directions (*loc. cit.*) gave, without further purification, a homogeneous product consisting of almost pure toxicaric acid, m. p. 206° (decomp.).

6 : 7-*Dimethoxychroman*-4-*carboxylic Acid* (*Netoric Acid*) (VI).—Reduction of ethyl 6 : 7-dimethoxy-3-acetoxy-Δ^3-chromene-4-carboxylate (1 g.), dissolved in acetic acid (25 c.c.), was effected with a platinum oxide catalyst (0·1 g.) and hydrogen at room temperature and a pressure of 60 lb./sq. in. in the course of 5 hours. After the separation of the catalyst ice was added, the acetic acid neutralised with sodium carbonate, and the product isolated with ether and hydrolysed by heating with 75% aqueous alcohol (15 c.c.) containing potassium hydroxide (1 g.) on the steam-bath for 1 hour. The mixture was diluted with water (15 c.c.), the greater part of the alcohol evaporated, and the residue acidified with hydrochloric acid. The resulting netoric acid (0·7 g.), which separated in the course of 24 hours, was recrystallised from hot water, forming the hydrate in colourless rods, m. p. 90—91° (rapid heating) (Found in air-dried material: C, 56·3; H, 6·3. Calc. for $C_{12}H_{14}O_5,H_2O$: C, 56·2; H, 6·3%). When slowly heated, this compound loses water with softening at about 90° and then melts sharply at 132—133°. Anhydrous material results when the hydrate is dried for 24 hours over phosphoric oxide in a vacuum at room temperature; m. p. 132—133° (Found : C, 60·8; H, 6·1. Calc. for $C_{12}H_{14}O_5$: C, 60·5; H, 5·9%). The hydrated and the anhydrous form were identical with specimens obtained by the hydrogenation of natural toxicaric acid by means of a platinum oxide catalyst; m. p. and mixed m. p. 90° and 132—133° respectively.

Esterification of the anhydrous acid with excess of ethereal diazomethane gave rise to the methyl ester, which separated from light petroleum (b. p. 40—60°) in clusters of slender needles, m. p. 60—61°, identical with the natural product (Takei and co-workers, *loc. cit.*) (Found : C, 61·9; H, 6·4. Calc. for $C_{13}H_{16}O_5$: C, 61·9; H, 6·4%).

Cyclisation of Derric Acid with Acetic Anhydride.—The acid (1·3 g.) was refluxed with acetic anhydride (20 c.c.) and sodium acetate (2 g.) for 15 minutes, and the pale brown mixture poured into water. Two days later the brownish solid (0·8 g.) was collected, dried, and extracted with warm light petroleum (b. p. 60—80°). The *product*, which slowly separated from the cooled extracts, was crystallised from aqueous methyl alcohol (charcoal) and then light petroleum, forming clusters of colourless slender prisms, m. p. 85° (Found : C, 62·5; H, 5·7. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6%). A cooled solution of this compound (0·2 g.) in alcohol (7 c.c.) was mixed with 8% aqueous sodium hydroxide (5 c.c.), kept at 25° for 5 minutes, acidified with dilute hydrochloric acid, and extracted with ether. Evaporation of the ether left a colourless crystalline solid, which in alcoholic solution gave a bright yellow precipitate instantaneously with aqueous dinitrophenylhydrazine hydrochloride (Brady's reagent). This prodnct, which is sparingly soluble in the usual organic solvents, separated from a large volume of hot acetic acid in brownish-orange boat-shaped prisms, decomposing at 203—204°.

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47. *Hydroxy-carbonyl Compounds. Part X. Coumarins and Chromones from* m-4-*Xylenol.*

By Daniel G. Flynn and Alexander Robertson.

In the present work it has been found that the condensation of *m*-4-xylenol with ethyl acetoacetate and its α-methyl and α-ethyl substitution products gives (a) coumarins by the method of Pechmann and (b) chromones by that of Simonis, with ethyl α-benzylacetoacetate and with ethyl benzoylacetate the Simonis reaction failed to yield condensation products, and the use of methyl- or ethyl-alcoholic hydrogen chloride in place of sulphuric acid in the Pechmann method gave disappointing yields of the coumarins (compare Crabtree, Robinson, and Turner, J., 1918, **113**, 879; Appel, J., 1935, 1031).

The methods employed to establish the coumarin and the chromone structure place the constitution of the products in question beyond doubt and in this connexion we have studied the application of the Kostanecki reaction to 2-hydroxy-3 : 5-dimethylacetophenone, using the anhydrides and sodium salts of acetic, propionic, and benzoic acids. With acetic anhydride and sodium acetate the three possible products are formed—2 : 6 : 8-*trimethylchromone* and its 3-acetyl derivative (isolated as the *oxime*) together with 4 : 6 : 8-trimethylcoumarin. Propionylation of this ketone affords a mixture in which only 3 : 4 : 6 : 8-tetramethylcoumarin (converted into 2-*methoxy*-α : β : 3 : 5-*tetramethylcinnamic acid*) and 3-propionyl-6 : 8-dimethyl-2-ethylchromone (isolated as the *oxime*) can be detected, although the presence of 6 : 8-*dimethyl*-2-*ethylchromone* is not excluded. Benzoylation, on the other hand, gives only 3-*benzoyl*-6 : 8-*dimethylflavone*.

The results obtained with the Kostanecki reaction fall into line with those described by Wittig (*Ber.*, 1924, **57**, 88; *Annalen*, 1925, **446**, 155) and by Heilbron and his co-workers (J., *1933, 1263; 1934, 1311, 1581*) in their more extensive investigations in this field. These authors have clearly shown that the course of the Kostanecki reaction is uncertain and therefore by itself cannot be relied upon to establish chromone structure. Nevertheless in certain cases arising in the course of the present series of investigations this reaction has a limited use and affords clear evidence on this point, *e.g.*, the compound obtained by the condensation of *m*-4-xylenol with ethyl α-methylacetoacetate by the method of Simonis is identical with the only product formed by the vigorous acetylation of 2-*hydroxy*-3 : 5-*dimethylpropiophenone* and therefore can only be 2 : 3 : 6 : 8-*tetramethylchromone*, confirmed by conversion into 2-(3′ : 4′-*methylenedioxystyryl*)-3 : 6 : 8-*trimethylchromone*. This would be equally true if, in addition to the chromone, the Kostanecki reaction had simultaneously given rise to isomeric 6 : 8-dimethyl-4-ethylcoumarin.

Experimental.

2-*Methoxy*-β : 3 : 5-*trimethylcinnamic Acid*.—Condensation of *m*-4-xylenol (10 g.) with ethyl acetoacetate (13 c.c.) by 86% sulphuric acid (80 c.c.) during 3 days gave 4 : 6 : 8-trimethylcoumarin, which formed needles (15 g.), m. p. 114—114·5°, from light petroleum (b. p. 40—60°) or aqueous alcohol (Clayton, J., 1908, **93**, 2019, gives m. p. 116—117°). Prepared from the coumarin (5·8 g.) by the standard procedure of Canter and Robertson (J., 1931, 1875), the *cinnamic acid* separated from light petroleum (b. p. 60—80°) in colourless rhombic plates (4·5 g.), m. p. 139° (Found: C, 71·0; H, 7·6. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). Oxidation of this acid according to Canter and Robertson's directions (*loc. cit.*) yielded 2-methoxy-3 : 5-dimethylacetophenone, characterised by the *semicarbazone*, m. p. 193°, identical with an authentic specimen (Found: C, 61·5; H, 7·3; N, 17·4. $C_{12}H_{17}O_2N_3$ requires C, 61·2; H, 7·3; N, 17·8%).

2-Methoxy-3 : 5-dimethylacetophenone (oil, b. p. 134—135°/21 mm.) was obtained by the methylation of 2-hydroxy-3 : 5-dimethylacetophenone (Auwers and Mauss, *Annalen*, 1928, **464**, 311) with methyl iodide and potassium carbonate in boiling acetone during 16 hours; the semicarbazone formed plates, m. p. 193°, from benzene–ligroin (Found: C, 61·4; H, 7·2; N, 17·7%).

2-*Methoxy*-α : β : 3 : 5-*tetramethylcinnamic Acid*.—3 : 4 : 6 : 8-Tetramethylcoumarin, m. p. 108° (Clayton, *loc. cit.*, gives m. p. 110—111°), yielded the *acid*, which formed colourless rectangular prisms from light petroleum (b. p. 60—80°), m. p. 139·5—140° (Found: C, 72·1; H, 7·8.

$C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). On oxidation, the acid gave 2-methoxy-3 : 5-dimethylacetophenone (semicarbazone, m. p. and mixed m. p. 193°).

4 : 6 : 8-*Trimethyl-3-ethylcoumarin* crystallised from 60% alcohol in clusters of needles, m. p. 112·5—113° (Found : C, 77·7; H, 7·3. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%). It is considerably more stable to boiling 14% aqueous methyl-alcoholic potassium hydroxide than either 4 : 6 : 8-trimethyl- or 3 : 4 : 6 : 8-tetramethyl-coumarin; conversion into the *o*-hydroxycinnamic acid was not complete after 12½ hours. Under similar conditions the latter coumarins are completely converted into the corresponding cinnamic acids after 3 hours.

Prepared by the standard method, 2-*methoxy*-β : 3 : 5-*trimethyl*-α-*ethylcinnamic acid* crystallised from light petroleum (b. p. 60—80°) in plates, m. p. 112° (Found : C, 72·6; H, 7·9. $C_{15}H_{20}O_3$ requires C, 72·6; H, 8·1%). On oxidation it gave 2-methoxy-3 : 5-dimethylacetophenone (semicarbazone, m. p. and mixed m. p. 193°).

4-*Phenyl*-6 : 8-*dimethylcoumarin* was obtained from *m*-4-xylenol (4 g.) and ethyl benzoylacetate (4 g.) with 86% sulphuric acid (32 c.c.), forming colourless needles (4 g.) from 80% alcohol, m. p. 111° (Found : C, 81·8; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

Replacement of ethyl benzoylacetate with ethyl α-benzylacetoacetate gave rise to 3-*benzyl*-4 : 6 : 8-*trimethylcoumarin*, which formed colourless needles (4·5 g.) from aqueous alcohol, m. p. 112—113° (Found : C, 82·1; H, 6·6. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

2 : 6 : 8-*Trimethylchromone*.—(A) 2-Hydroxy-3 : 5-dimethylacetophenone (6 g.) was heated with ethyl acetate (15 c.c.) and sodium (3 g. in small pieces) on the steam-bath for 4 hours; further quantities of ester (50 c.c.) and sodium (2·3 g.) were added after 1½ hours. Acidification of a solution of the cold homogeneous reaction mixture in water with acetic acid precipitated 2-*hydroxy*-ω-*acetyl*-3 : 5-*dimethylacetophenone*, which crystallised from dilute alcohol in colourless needles (4·5 g.), m. p. 85°, giving a red ferric chloride reaction (Found : C, 69·6; H, 6·5. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). Cyclisation of this compound in warm acetic acid containing a little hydrochloric acid produced a quantitative yield of the *chromone*, forming colourless prisms from ether, m. p. 125° (Found : C, 77·0; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·7; H, 6·4%).

(B) An intimate mixture of *m*-4-xylenol (5 g.), ethyl acetoacetate (5 g.), and phosphoric oxide (7·5 g.) was heated on the steam-bath for 2 hours; after 1 hour, more oxide (7·5 g.) was added. The product was isolated from a cold alkaline digest of the reaction mixture with much ether, distilled in a high vacuum, and crystallised from ether (yield, 1—1·5 g.), m. p. and mixed m. p. 125° (Found : C, 76·9; H, 6·5%). Condensation of this compound (0·5 g.) and piperonal (0·38 g.) with boiling alcoholic sodium ethoxide (0·06 g. of metal in 15 c.c.) for 1½ hours gave 2-(3′ : 4′-*methylenedioxystyryl*)-6 : 8-*dimethylchromone*, which separated from warm alcohol in pale yellow prisms, m. p. 195° (Found : C, 75·1; H, 5·1. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

2-*Hydroxy*-3 : 5-*dimethylpropiophenone*.—The propionate of *m*-4-xylenol was prepared from the phenol with propionic anhydride and pyridine; b. p. 124—125°/20 mm. (compare Palfray and Duboi, *Compt. rend.*, 1927, **185**, 1479). When the vigorous reaction between this ester (10 g.) and aluminium chloride (15 g., added gradually) had subsided, the mixture was maintained at 130—140° for 5 hours; the *ketone*, isolated in the usual manner, formed colourless plates (9 g.), m. p. 52—53°, from dilute alcohol and gave a deep blue ferric chloride reaction (Found : C, 74·0; H, 8·0. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%).

2 : 3 : 6 : 8-*Tetramethylchromone*.—Vigorous acetylation of the foregoing ketone (3 g.) with sodium acetate (5 g.) and acetic anhydride (30 c.c.) at 180° for 22 hours yielded the *chromone* (1·6 g.), which formed needles from ether, m. p. 136—137° (Found : C, 77·4; H, 6·7. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%). The same compound (1·4 g.) was obtained by the condensation of ethyl α-methylacetoacetate (5 g.) with *m*-4-xylenol (5 g.) by means of phosphoric oxide (15 g.) at 100° during 3 hours; m. p. and mixed m. p. 136—137° (Found : C, 77·4; H, 6·8%). Prepared in the usual manner, 2-(3′ : 4′-*methylenedioxystyryl*)-3 : 6 : 8-*trimethylchromone* separated from alcohol in yellow needles, m. p. 196° (Found : C, 75·2; H, 5·5. $C_{21}H_{18}O_4$ requires C, 75·4; H, 5·4%).

2-*Hydroxy*-3 : 5-*dimethyl*-n-*butyrophenone*.—Treatment of *m*-4-xylenol (15 g.) with *n*-butyryl chloride (15 c.c.) and pyridine (17 c.c.) on the steam-bath gave the *butyrate*, a colourless oil (20 g.), b. p. 132—133°/17·5 mm. (Found : C, 74·8; H, 8·6. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The Fries reaction on this ester is best carried out at 110—115° (6·5 hours), and the *ketone* purified by distillation, b. p. 145—150°/30 mm., m. p. 30° (Found : C, 75·1; H, 8·4%); yield, 84% of the theoretical. It gives a deep blue ferric chloride reaction.

2 : 6 : 8-*Trimethyl-3-ethylchromone*, obtained by the application of the Simonis reaction to *m*-4-xylenol and the requisite ester (3 hours at 100°), separated from ether in colourless needles, m. p. 112·5° (Found : C, 78·0; H, 7·7. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%). Mixed with

4 : 6 : 8-trimethyl-3-ethylcoumarin, it melted at about 92°. The same chromone appeared to be the only product formed by acetylation of 2-hydroxy-3 : 5-dimethyl-*n*-butyrophenone at 180° for 18 hours; m. p. and mixed m. p. 112·5°. Prepared from this compound, 2-(3′ : 4′-*methylenedioxystyryl*)-6 : 8-*dimethyl*-3-*ethylchromone* crystallised from alcohol in pale yellow needles, m. p. 202—203° (Found : C, 75·7; H, 5·9. $C_{22}H_{20}O_4$ requires C, 75·8; H, 5·8%).

Acetylation of 2-*Hydroxy*-3 : 5-*dimethylacetophenone*.—The ketone (20 g.) was heated with acetic anhydride (50 c.c.) and sodium acetate (20 g.) at 170° for 6 hours and then at 200° for 14 hours, and the reaction product (18 g.) isolated in the usual manner. A solution of hydroxylamine hydrochloride (2·5 g.) and sodium acetate (2·5 g.) in water (25 c.c.) was added to a part of this material (5 g.) dissolved in acetic acid (25 c.c.) and the mixture was refluxed for 5 minutes, diluted with water, and neutralised with sodium carbonate. Next day the solid was collected, washed, and extracted with ten portions (10 c.c. each) of 5% aqueous sodium hydroxide, an insoluble residue being left. Acidification of the combined extracts with hydrochloric acid precipitated the *oxime* of 3-acetyl-2 : 6 : 8-trimethylchromone, which separated from methyl alcohol in rectangular plates (1·5 g.), m. p. 119° (Found : C, 68·6; H, 6·4; N, 5·7. $C_{14}H_{15}O_3N$ requires C, 68·6; H, 6·1; N, 5·7%).

A dried ethereal solution of the residue left on removal of the oxime was saturated with hydrogen chloride and the resulting precipitate of the hydrochloride of 2 : 6 : 8-trimethylchromone was collected and decomposed with aqueous sodium carbonate. The chromone (1·8 g.), m. p. 125° after purification, was identical with an authentic specimen.

A solution of the crude reaction mixture (10 g.) in methyl alcohol (50 c.c.) and 25% aqueous sodium hydroxide (40 c.c.) was refluxed for 2 hours, cooled, diluted with water, filtered from insoluble material, and acidified with hydrochloric acid. Next day the solid was collected and digested with aqueous sodinm bicarbonate, and the insoluble residue submitted to the process nsed for the conversion of 4 : 6 : 8-trimethylcoumarin into 2-methoxy-β : 3 : 5-trimethylcinnamic acid. The resulting product (0·4 g.) was identical with the latter cinnamic acid, m. p. and mixed m. p. 139—139·5° after crystallisation from light petroleum.

6 : 8-*Dimethyl*-2-*ethylchromone*.—A mixture of 2-hydroxy-3 : 5-dimethylacetophenone (6 g.), ethyl propionate (25 c.c.), and sodium (3 g., in small pieces) was refluxed for 3 hours (the solution became green and then brown), the cooled mixture acidified with acetic acid, and the unchanged ester and ketone removed in a current of steam. A solution of the residual solid (ferric chloride reaction negative) in warm light petroleum (b. p. 60—80°) deposited the *chromone* in elongated plates, m. p. 109—110° (Found : C, 77·1; H, 6·7. $C_{13}H_{14}O_2$ requires C, 77·3; H, 7·0%). Attempts to isolate the intermediate diketone were unsuccessful.

Propionylation of 2-*Hydroxy*-3 : 5-*dimethylacetophenone*.—A mixture of the ketone (20 g.), propionic anhydride (70 c.c.), and sodium propionate (40 g.) was heated at 160°, then to 210° in the course of 4 hours, and maintained at this temperature for 10½ hours. After isolation, the oily product (15 g.) was distilled in a high vacuum, b. p. 160—172°/1 mm., and then crystallised from light petroleum; m. p. 84—86° after softening at 78°. A solution of this material (0·5 g.) in methyl alcohol (4 c.c.) and 25% aqueous sodium hydroxide (4 c.c.) was refluxed for 3 hours, cooled, diluted with water, filtered, and acidified with hydrochloric acid, yielding a mixture, which, by means of aqueous sodium bicarbonate, was resolved into 3 : 4 : 6 : 8-tetramethylcoumarin, m. p. and mixed m. p. 108° after crystallisation from dilute alcohol, and an acid. The latter separated from benzene in colourless rods, m. p. 179°, giving a blue ferric chloride reaction and was identical with 2-hydroxy-3 : 5-dimethylbenzoic acid (Found : C, 65·2; H, 6·0. Calc. for $C_9H_{10}O_3$: C, 65·1; H, 5·9%).

Oximation of the crnde reaction mixture, m. p. 84—86° (6 g.), with an aqueous solution of hydroxylamine (4 g. in 30 c.c.), first at 100° for 15 minutes and then at room temperature for 4 days, gave the *oxime* of 3-propionyl-6 : 8-dimethyl-2-ethylchromone, which was isolated by extraction of the crude product with 5% aqueous sodium hydroxide and acidification of the combined extracts. This derivative separated from methyl alcohol in diamond-shaped plates, m. p. 93° (Found : C, 70·1; H, 6·9; N, 5·3. $C_{16}H_{19}O_3N$ requires C, 70·3; H, 7·0; N, 5·1%).

3-*Benzoyl*-6 : 8-*dimethylflavone*.—Benzoylation of 2-hydroxy-3 : 5-dimethylacetophenone (5 g.) with benzoic anhydride (25 g.) and sodium benzoate (5 g.) at 180—190° for 16 hours and subsequent treatment of the reaction mixture with water and then sodium hydroxide gave rise to the *flavone*, which formed almost colourless, rectangular plates from alcohol, m. p. 191—192° (Found : C, 81·0; H, 5·2. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1%).

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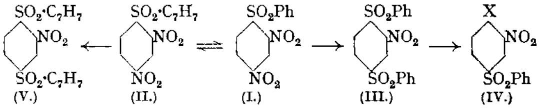
48. The Action of Sulphinates on 2 : 4-Dinitrodiphenylsulphones.

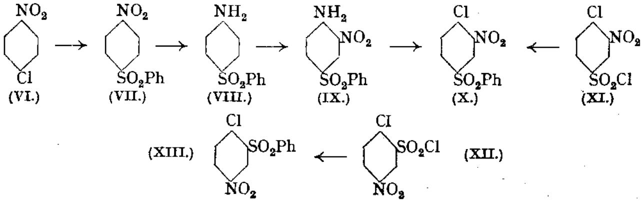
By James D. Loudon.

It has previously been shown (Loudon, J., 1935, 537) that the action of sodium *p*-toluenesulphinate on 2 : 4-dinitrodiphenylsulphone results in a rapid and reversible exchange of sulphonyl groups (I ⇌ II), accompanied by slower secondary reactions of unknown nature, apparently incurred by the continued action upon (I) and (II) of sulphinate present in excess or produced during the exchange. To avoid unnecessary complications in investigating this second phase, the action of sodium benzenesulphinate on 2 : 4-dinitrodiphenylsulphone (I) was first examined. Analysis of the isolated product indicated a nitrobis(phenylsulphonyl)benzene structure (*e.g.*, III), and its reactions showed the presence of one mobile phenylsulphonyl group. For instance, with alcoholic alkali a mixture of a *phenol* (IV; X = OH) and its *ethyl* ether (X = OEt) was readily produced, and alcoholic ammonia and piperidine gave an *amine* ($X = NH_2$) and a *piperidino*-derivative ($X = NC_5H_{10}$) respectively.



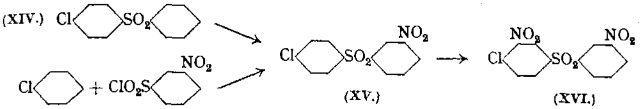
Since the mobility of this phenylsulphonyl group is comparable with that in (I), the inference may be drawn that it arises from the combined activating influences of both the residnal nitro- and the second phenylsulphonyl group (for the activating effect of analogous combinations upon halogens, cf. *inter alia* Le Fèvre and Turner, J., 1927, 1113), and hence that the formation of the disulphonyl compound from (1) probably consists in replacement of one or other nitro-group by phenylsulphonyl (contrast the action of potassium cyanide on 2 : 4-dinitrochlorobenzene, where CN enters position 3; Van Heteren, *Rec. trav. chim.*, 1901, **20**, 107; Blanksma, *ibid.*, 1902, **21**, 424).

The selection of the *p*-nitro-group in (I) as the group actually concerned in the replacement follows from synthetic evidence, *viz.*, the mononitro-derivative (IX) of *p*-aminodiphenylsulphone was identical with the amine obtained from (III) with alcoholic ammonia, and was converted into the *chloronitro*-compound (X), from which (III) and its reaction products (IV) were produced by treatment with the appropriate reagents. Further, (X) was also obtained from the Friedel–Crafts condensation between 4-chloro-3-nitrobenzenesulphonyl chloride (XI) and benzene, whereas the isomeric *compound* (XIII), obtained in a similar way from (XII), yielded a *piperidino*-derivative quite distinct from (IV) ($X = NC_5H_{10}$).

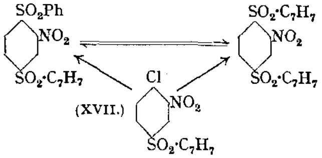


A parallel series of reactions and synthesis similarly identified the product of the action of sodium *p*-toluenesulphinate on (II) as 1-*nitro*-2 : 5-*di*-p-*tolylsulphonylbenzene* (V), but in this series the condensation between (XI) and toluene gave unworkable products. In both series the projected formation of the chloronitro-compounds by mononitration of

p-chlorodiphenylsulphone (XIV) and *p*-chlorophenyl-*p*-tolylsulphone was frustrated by entrance of the nitro-group into the non-halogenated nucleus, as shown by the absence of halogen mobility in the product (XV) (piperidine test) and by an independent preparation.



This result is analogous to the heteronuclear nitration of monohalogenated diphenyl derivatives, but the more closely related case of the benzophenone class does not appear to have been investigated. Dinitration of (XIV) yielded the active *chloro*-compound (XVI), from which a *piperidino*-derivative and the corresponding *amine* were readily obtainable. The disulphonyl derivatives obtained from (X), from its *p*-tolyl analogue (XVII), and from (XVI), all displayed the capacity to exchange sulphonyl groups adjacent to the nitro-group, but this capacity was less marked than in the case of the 2 : 4-dinitrodiphenylsulphones.



These results sufficiently indicate one aspect of the changes involved in the action of sulphinates on 2 : 4-dinitrodiphenylsulphones—others, which probably originate in the reducing powers of the sulphinates, have not been investigated. Whilst, as might be expected, replacement of the mobile nitro-group by arylsulphonyl was found to occur in both *o*- and *p*-dinitrobenzenes under the conditions employed for reaction with the corresponding chloronitro-compounds, the replacement of the *p*-nitro-groups in (I) and (II) involves some special features requiring further investigation. In this connexion, however, two points deserve mention : (1) in general, sulphinates may be expected to differ from the usual reagents (amines, hydroxides, etc.) employed to detect mobility in nitro-compounds, in that the latter, by introducing NH_2, OH, etc., tend to neutralise the effect of the nitro-group in facilitating further attack by anions, and (2) in particular, neither the nitro-group in (VII) nor that in the *o*-isomeride is replaced under the conditions sufficient to effect the replacements (I ⟶ III), (II ⟶ V).

Experimental.

1-*Nitro*-2 : 5-*diphenylsulphonylbenzene* (III).—A solution of 2 : 4-dinitrodiphenylsulphone (5 g.) and sodium benzenesulphinate (10 g.) in hot aqueous dioxan was refluxed for 3—4 hours. The semi-solid mass which separated on cooling or on addition of water was washed with alcohol, then with water, and crystallised from acetic acid, forming colourless felted needles, m. p. 157—158°, soluble without decomposition in warm concentrated sulphuric acid and only very slowly attacked by aqueous alkali. The same *compound* was obtained by boiling the reagents for a few minutes in ethylene glycol solution (Found : C, 53·5; H, 3·5; N, 3·8; S, 16·1. $C_{18}H_{13}O_6NS_2$ requires C, 53·6; H, 3·3; N, 3·5; S, 15·9%).

3-*Nitro*-4-*piperidinodiphenylsulphone* (IV, X = NC_5H_{10}) was prepared by dissolving (III) in boiling piperidine, followed by dilution with water, extraction of the precipitate with hot concentrated hydrochloric acid, and reprecipitation with water. It formed salmon-coloured plates, m. p. 133°, from alcohol (Found : N, 7·9. $C_{17}H_{18}O_4N_2S$ requires N, 8·1%).

Action of Aqueous-alcoholic Alkali on (III).—A suspension of (III) (0·4 g.) in alcohol (15 c.c.)

and 3% aqueous caustic soda (4 c.c.) was refluxed till complete dissolution was effected. After partial removal of the alcohol, addition of water yielded an oil, which slowly solidified and was found to be *3-nitro-4-ethoxydiphenylsulphone*; it formed needles, m. p. 147°, from alcohol (Found : N, 4·65. $C_{14}H_{13}O_5NS$ requires N, 4·8%). The filtrate from this substance gave on acidification with acetic acid *3-nitro-4-hydroxydiphenylsulphone*, which crystallised from alcohol in almost colourless plates, m. p. 137° (Found : N, 5·1. $C_{12}H_9O_5NS$ requires N, 5·0%).

*1-Nitro-2 : 5-di-*p*-tolylsulphonylbenzene* (V), prepared in the same manner as (III), had similar appearance and properties. M. p. 220—221° (Found : C, 56·1 ; H, 4·3 ; N, 3·4 ; S, 15·0. $C_{20}H_{17}O_6NS_2$ requires C, 55·7 ; H, 3·9 · N, 3·3 ; S, 14·85%).

3-Nitro-4-piperidino-4'-methyldiphenylsulphone was obtained in two forms—rapid crystallisation of the crude product [preparation similar to (IV) above] from hot alcohol yielding one form, m. p. 96—97°, which, kept in contact with the solvent, changed to the second form, m. p. 107—108°, also obtained directly by slower crystallisation (Found : N, 7·95. $C_{18}H_{20}O_4N_2S$ requires N, 7·8%).

3-Nitro-4-hydroxy-4'-methyldiphenylsulphone, m. p. 157—158° (Found : N, 4·9. $C_{13}H_{11}O_5NS$ requires N, 4·8%), and its *ethyl* ether, m. p. 143—144° (Found : N, 4·2. $C_{15}H_{15}O_5NS$ requires N, 4·4%), were prepared as in the cases of their lower homologues.

Mononitrodiphenylsulphones.—The following procedure dispenses with the sealed tubes employed in two instances by Ullmann and Pasdermadjian (*Ber.*, 1901, **34**, 1150). The requisite chloronitrobenzene and sodium sulphinate in molecular proportion were boiled in ethylene glycol for 3—4 hours. The product which separated on cooling (or on addition of water) was washed with alcohol and water and crystallised (charcoal) from alcohol or acetic acid. *o*-Nitrodiphenylsulphone had m. p. 147° (Found : N, 5·3. Calc. : N, 5·3%). *p*-Nitrodiphenylsulphone had m. p. 143° (Found : N, 5·4%). 2-Nitro-4'-methyldiphenylsulphone had m. p. 156° (*Chem. Abs.*, 1933, 998, patent, gives m. p. 156—157°) (Found : N, 5·2%).

4-Nitro-4'-methyldiphenylsulphone had m. p. 170° (Found : N, 5·2. $C_{13}H_{11}O_4NS$ requires N, 5·05). *o*- and *p*-Dinitrobenzenes (0·5 g.), treated in the same way for 30—40 minutes, gave the corresponding sulphones (m. p. and mixed m. p.).

4-Amino-4'-methyldiphenylsulphone (for indirect preparation, cf. Halberkmann, *Ber.*, 1922, **55**, 3074).—The nitro-sulphone (6 g.) was added in small quantities at a time to a boiling solution of stannous chloride (15 g.) in alcohol (15 c.c.) and the resulting solution after addition of concentrated hydrochloric acid (15 c.c.) was cooled and slowly stirred into 300 c.c. of 20% caustic soda solution. The precipitated amine was repeatedly extracted with alcohol and was crystallised from the same solvent; m. p. 181° (Found : N, 5·6. Calc. : N, 5·7%). 2-Amino-4'-methyldiphenylsulphone, similarly prepared, had m. p. 120—121° (Halberkmann, *loc. cit.*, gives m. p. 120—121°) (Found : N, 5·7%).

3-Nitro-4-aminodiphenylsulphone (IX).—(*A*) *p*-Aminodiphenylsulphone (Ullmann and Pasdermadjian, *loc. cit.*) was converted into the *p-toluenesulphonamide*, m. p. 190° (from acetic acid), by treatment with *p*-toluenesulphonyl chloride and pyridine (Found : N, 4·0. $C_{19}H_{17}O_4NS_2$ requires N, 3·6%). The sulphonamide (6 g.) was heated with nitric acid (6 c.c.; *d* 1·4) in acetic acid solution (60 c.c.) for 1 hour; on cooling, *3-nitro-4-*p*-toluenesulphonamidodiphenylsulphone* crystallised, m. p. 171° (from acetic acid) (Found : N, 6·8. $C_{19}H_{16}O_6N_2S_2$ requires N, 6·5%). Hydrolysis by warm concentrated sulphuric acid yielded the required *amine*, m. p. 169—170° from acetic acid (Found : N, 9·9. $C_{12}H_{10}O_4N_2S$ requires N, 10·1%).

(*B*) 1-Nitro-2 : 5-diphenylsulphonylbenzene (0·5 g.), methyl alcohol (5 c.c.), and concentrated ammonia solutiou (0·6 c.c.) were heated in a sealed tube at 130° for 5 hours. The yellow crystalline product had m. p. 168—169° (from acetic acid), undepressed by admixture with the amine from (*A*).

3-Nitro-4-amino-4'-methyldiphenylsulphone.—(*A*) 4-Amino-4'-methyldiphenylsulphone yielded the *p-toluenesulphonamide*, m. p. 213—214° (from acetic acid) (Found : N, 3·8. $C_{20}H_{19}O_4NS_2$ requires N, 3·5%). From the nitration solution [the amide (8 g.), acetic acid (80 c.c.), and nitric acid (6 c.c.; *d* 1·4) after 1 hour's refluxing] there separated *3 : 5-dinitro-4-*p*-toluenesulphonamido-4'-methyldiphenylsulphone* in colourless felted needles, m. p. 221° (Found : N, 8·25. $C_{20}H_{17}O_8N_3S_2$ requires N, 8·5%), which was hydrolysed to *3 : 5-dinitro-4-amino-4'-methyldiphenylsulphone*, yellow needles (from acetic acid), m. p. 216° with previous softening at 205° (Found : N, 12·4. $C_{13}H_{11}O_6N_3S$ requires N, 12·5%). The constitution of this compound follows from its non-identity with 3 : 3'-dinitro-4-amino-4'-methyldiphenylsulphone (cf. below). The mother-liquor of the nitration solution after removal of the dinitro-compound gave on dilution with water *3-nitro-4-*p*-toluenesulphonamido-4'-methyldiphenylsulphone*, m. p. 129—130° after repeated crystallisation from alcoholic dioxan (Found : N, 6·4. $C_{20}H_{18}O_6N_2S_2$

requires N, 6·3%). Hydrolysis of this product with concentrated sulphuric acid yielded the required *amine* (yellow needles, m. p. 184°, from acetic acid).

(*B*) The same amine (m. p. and mixed m. p. 184—185°) was obtained from (V) and alcoholic ammonia in the way already described for the phenyl homologue (Found : N, 9·7. $C_{18}H_{12}O_4N_2S$ requires N, 9·6%).

4-*Chloro*-3-*nitrodiphenylsulphone* (X).—(*A*) 3-Nitro-4-aminodiphenylsulphone was subjected to Hodgson and Walker's modification of the Sandmeyer reaction (J., 1933, 1620). The product formed pale yellow needles, m. p. 127°, from alcoholic dioxan. (*B*) 4-Chloro-3-nitrobenzenesulphonyl chloride, prepared by nitration of *p*-chlorobenzenesulphonyl chloride as described by Davies and Wood (*J.*, 1928, 1125) but with the use of nitric acid (*d* 1·53), melted at 61—62° (from light petroleum) instead of 39—40° (*loc. cit.*). Fischer (*Ber.*, 1891, **24**, 3188) gives m. p. 40—41°, whereas Pollak and Katscher (*Monatsh.*, 1930, **55**, 371) find the value 59—60° (Found : N, 5·4. Calc. : N, 5·5%). The sulphonyl chloride (6 g.), aluminium chloride (6 g.), and benzene (10 c.c.) were heated on the water-bath for 1 hour. The semi-solid mass obtained on cooling and addition to water was extracted with hot acetic acid, from which the required product separated, m. p. and mixed m. p. with (*A*) 125—126° after purification (Found : N, 4·8. $C_{12}H_8O_4NClS$ requires N, 4·7%). Treatment with piperidine in the usual way gave the piperidino-derivative (IV; $X = NC_5H_{10}$), m. p. and mixed m. p. with the piperidino-compound prepared from (II) 132—133°. Digestion with aqueous alkali yielded the phenol, m. p. and mixed m. p. 137°, and with alcoholic sodium ethoxide, the ethyl ether, m. p. and mixed m. p. 147—148°.

4-*Chloro*-3-*nitro*-4′-*methyldiphenylsulphone* was prepared as described for (X, *A*) and gave corresponding halogen replacements; m. p. 120° (from alcohol) (Found : N, 4·6. $C_{13}H_{10}O_4NClS$ requires N, 4·5%).

2-*Chloro*-5-*nitrodiphenylsulphone* (XIII) was prepared from the sulphonyl chloride (XII) in the usual way (cf. X, *B*) and crystallised from dioxan in long silky needles, m. p. 174° (Found : N, 4·9. $C_{12}H_8O_4NClS$ requires N, 4·7%). Treatment with piperidine gave 5-*nitro*-2-*piperidinodiphenylsulphone* in yellow plates, m. p. 178° (Found : N, 8·1. $C_{17}H_{18}O_4N_2S$ requires N, 8·1%).

4-*Chloro*-3′-*nitrodiphenylsulphone* (XV).—(*A*) Solutions of 4-chlorodiphenylsulphone (2·5 g.) and potassium nitrate (1 g.) in concentrated sulphuric acid (5 c.c. each) were mixed at 10° and, after 12 hours, poured into water. The solid was crystallised repeatedly from acetic acid. (*B*) *m*-Nitrobenzenesulphonyl chloride (2 g.), chlorobenzene (3 c.c.), and aluminium chloride (2 g.), treated in the usual way, gave the same *product* in colourless needles, m. p. 139—140° (Found : N, 4·9. $C_{12}H_8O_4NClS$ requires N, 4·7%).

4-*Chloro*-3 : 3′-*dinitrodiphenylsulphone* (XVI) was prepared in similar fashion from the mononitro-sulphone (XV) (3 g.), sulphuric acid (9 c.c.), and potassium nitrate (1 g.) or by direct dinitration; m. p. 146° (from acetic acid) (Found : N, 8·3. $C_{12}H_7O_6N_2ClS$ requires N, 8·2%). The *piperidino*-derivative was obtained in salmon-coloured leaflets, m. p. 151—152° (Found : N, 10·7. $C_{17}H_{17}O_6N_3S$ requires N, 10·7%).

3 : 3′-*Dinitro*-4-*aminodiphenylsulphone*, prepared from (XVI) and methyl-alcoholic ammonia (cf. IX, *B*), had m. p. 238° (from ethylene glycol) (Found : N, 13·2. $C_{12}H_9O_6N_3S$ requires N, 13·0%).

The following compounds were prepared in a similar way from 4-chloro-4′-methyldiphenylsulphone : 4-*chloro*-3′-*nitro*-4′-*methyldiphenylsulphone*, m. p. 103° (Found : N, 4·6. $C_{13}H_{10}O_4NClS$ requires N, 4·5%); 4-*chloro*-3 : 3′-*dinitro*-4′-*methyldiphenylsulphone*, m. p. 152° (Found : N, 7·9. $C_{13}H_9O_6N_2ClS$ requires N, 7·85%); 3 : 3′-*dinitro*-4-*piperidino*-4′-*methyldiphenylsulphone*, m. p. 149—150° (Found : N, 10·4. $C_{18}H_{19}O_6N_3S$ requires N, 10·4%); and 3 : 3′-*dinitro*-4-*amino*-4′-*methyldiphenylsulphone*, m. p. 231° (Found : N, 12·5. $C_{13}H_{11}O_6N_3S$ requires N, 12·5%).

By heating equimolecular proportions of sodium benzene- or *p*-toluene-sulphinate in aqueous alcohol (or dioxan) with the requisite chloronitro-compound (X, XVI, XVII) for 30—60 minutes, the following disulphones were prepared; they were purified by crystallisation from acetic acid : 1-nitro-2 : 5-diphenylsulphonyl- and -2 : 5-di-*p*-tolylsulphonyl-benzene; 1-*nitro*-5-*phenylsulphonyl*-2-p-*tolylsulphonylbenzene*, m. p. 180° (Found : N, 3·6. $C_{19}H_{15}O_6NS_2$ requires N, 3·4%); 1-*nitro*-2-*phenylsulphonyl*-5-p-*tolylsulphonylbenzene*, m. p. 212° (Found : N, 3·5. $C_{19}H_{15}O_6NS_2$ requires N, 3·4%); 1-*nitro*-2-*phenylsulphonyl*-5-m-*nitrophenylsulphonylbenzene*, m. p. 233° (from *cyclo*hexanone) (Found : N, 6·4. $C_{18}H_{12}O_8N_2S_2$ requires N, 6·25%); and 1-*nitro*-5-m-*nitrophenylsulphonyl*-2-p-*tolylsulphonylbenzene*, m. p. 232° (Found : N, 6·0. $C_{19}H_{14}O_8N_2S_2$ requires N, 6·1%).

Exchanges between the 2-arylsulphonyl groups were effected in dioxan solution as previously described (*J.*, 1935, 537), the reactions here requiring 30 minutes' heating to attain equilibrium.

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49. *Mechanism of, and Constitutional Factors controlling, the Hydrolysis of Carboxylic Esters. Part VIII. Energies Associated with Induced Polar Effects in the Hydrolysis of Substituted Benzoic Esters.*

By CHRISTOPHER K. INGOLD and WILFRED S. NATHAN.

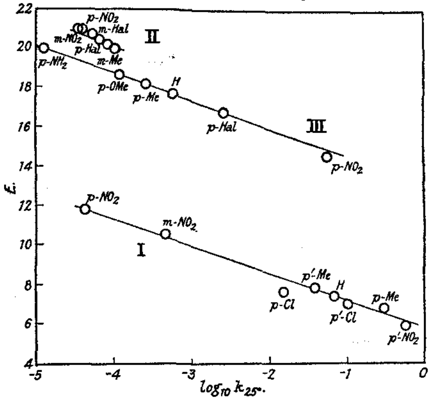
IT is a tacit assumption of the electronic theory of organic reactions that a substituent in modifying the availability of electrons at the site of a reaction thereby alters the energy of activation (*Chem. Reviews*, 1934, **15**, 227). The experimental examination of this proposition has already been taken up by several authors, using the only practicable method, *viz.*, analysis of the effects of constitution on reaction rate into effects on B and E in the Arrhenius equation $k = Be^{-E/RT}$ $(= PZe^{-E/RT})$. First, Bradfield and Jones (J., 1928, 1006, 3073; 1931, 2903, 2907) showed that in the nuclear halogenation of phenol ethers the changes of rate are controlled, mainly at least, by changes of critical energy which the substituents influence in an additive manner. Secondly, Nathan and Watson (J., 1933, 217, 890, 1248) showed that a similar assumption for aromatic side-chain reactions would lead to a simple connexion between the dipole moment of a group and its effect on the critical energy; however, Evans, Morgan, and Watson (J., 1935, 1168) measured Arrhenius critical energies for the acid-catalysed bromination of nuclear-substituted acetophenones and observed deviations which they regarded as sufficiently serious to deserve a special interpretation. Thirdly, Williams and Hinshelwood showed that the effect of nuclear substituents on the rate of benzoylation of anilines is, in fact, controlled almost wholly by the effect on E; however, in other studies by Hinshelwood, Winkler, and Legard, in which no use is made of the principle of isolating induced polarity from local effects by interposing the electrically conducting benzene ring between the substituent and the reaction zone, marked changes in both B and E were found (J., 1934, 1079; 1935, 587, 1147, 1588).

We have confined ourselves to the case in which induced polar effects may be assumed to be isolated from local disturbances: we have studied the alkaline hydrolysis of *p*-substituted benzoic esters, and have investigated in the usual way the dependence of changes in the absolute rate on variations of B and of E. Before considering our own results, however, we wish further to discuss the two prior investigations (one published during the progress of our experiments, and the other after their completion) in which the conditions and methods are similar to ours; for it has been suggested that these researches reveal a noteworthy difference of result, inasmuch as in Williams and Hinshelwood's experiments on the benzoylation of anilines the plot of E against $\log_{10}k$ approximated to a straight line of that slope $(-2{\cdot}303RT)$ which corresponds to constancy in B, whereas in Evans, Morgan, and Watson's experiments on the bromination of acetophenones no such plot was obtained. We take the view, however, that it is asking altogether too much of the Arrhenius equation to anticipate a linear plot of the right slope for the acetophenone experiments because of the smallness of the range of velocities. It is pointed out in another connexion (following paper) how unsatisfactory the conclusions can be which follow from an *exact* identification of Arrhenius's B and E, both of which are functions of temperature, with quantities implicitly considered to be functions of structure alone: such an identification is justified only when the differences in question are large. Now Williams and Hinshelwood had a range of variation of $1 : 10^4$ in k, and hence the Arrhenius

equation was adequate to establish the conclusion which these authors drew, *viz.*, that the changes of rate are correlated essentially with changes in the energy of activation. On the other hand, in Evans, Morgan, and Watson's experiments the extreme range of k was only 1 : 3, and the Arrhenius equation was therefore, in our opinion, not a sufficiently refined instrument of analysis.

Our results agree with those of Williams and Hinshelwood, but we made our range of variation of velocity as large as we could, *viz.*, 1 : 5000. The corresponding extreme range of the factor B was only 1 : 2·5, so that almost the whole of the variation of rate was accounted for by the alterations of E.

Effect of nuclear substituents on second-order rate constants of aromatic side-chain reactions.



[E is in kg.-cals., and $k_{25°}$ in l./g.-mol./sec. The lines represent B = constant.]

Series I : Benzoylation of anilines in benzene (W. and H.). Rate $\propto$[Ar·NH_2][Ar·COCl]. Substitution in aniline nucleus represented by *m*- and *p*-, and in benzoyl chloride nucleus by *p*′-.

Series II : Hydrion-catalysed bromination of acetophenones in 75% acetic acid (E., M., and W.). Rate $\propto$[$H^{\cdot}$][Ar·COMe]. The points for the separate halogens are so closely grouped that only mean points are given, one for the *m*- and one for *p*-halogens.

Series III : Saponification of benzoic esters in 85% ethyl alcohol (this paper). Rate $\propto$[OH'][Ar·CO_2Et]. The closely grouped points for the separate halogens are represented by a mean point.

In the figure the three aromatic side-chain reactions, (I) the benzoylation of anilines, (II) the hydrion-catalysed bromination of acetophenones, and (III) the saponification by hydroxide ion of ethyl benzoates, are compared with respect to the influence of nuclear substituents on k and on E and B : E is plotted against $\log_{10}k_{25°}$ on the same scale for the three reactions, and in each case a straight line of the slope which signifies the invariance of B is drawn through the point for the unsubstituted compound. It will be observed that the deviations of the points from the reference lines are comparable in the three cases; in particular, it is not apparent that the data for the acetophenone reaction are qualitatively distinct from, or in demonstrable conflict with the general trend of, the other results. Of course, if the acetophenone points are plotted on a scale large enough to make their locus as long as those which relate to the other two reactions, the deviations look very great.

The data for the saponification of benzoic esters are summarised in the following table, where the second-order rate constants at 25° are in l./g.-mol./sec. The sequence of groups is normal except amongst the halogens, where, however, the differences of rate are not

of a kind to which we should ascribe simple constitutional significance. The *p*-methoxy-group, although electron-attracting, is in its right place in the series for the reason already

p-Substituent.	$10^5 k_{25°}$.	*E* (cals.).	$10^{-9}B$.	*p*-Substituent.	$10^5 k_{25°}$.	*E* (cals.).	$10^{-9}B$.
NH_2	1·27	20,000	5·42	Cl	237	16,800	4·93
OMe	11·5	18,650	5·38	I	278	16,700	4·93
Me	25·1	18,200	5·73	Br	289	16,800	5·82
H	55·0	17,700	5·32	NO_2	5670	14,500	2·30

explained in relation to the strengths of the substituted benzoic acids (J., 1933, 1124); a *m*-methoxy-group would fall, of course, between H and *m*-Cl. Evidently, the reaction requires the recession of electrons, as we should expect from its electronic nature.

Experimental.

Materials.—Ethyl benzoate and its *p*-amino-, *p*-methoxy-, *p*-chloro-, *p*-bromo-, and *p*-nitro-derivatives were purchased, and the *p*-iodo-derivative was prepared from the amino-compound. All the liquid esters were purified by repeated fractionation, considerable head and tail fractions being neglected. The crystalline amino- and nitro-esters were crystallised from ethyl alcohol repeatedly, and further purified by partial freezing. In some preliminary experiments the medium was " 50% " aqueous alcohol, *i.e.*, 50 g. of absolute ethyl alcohol made up to 100 c.c. with water. In the main series the medium was " 85% " aqueous alcohol; this was made up by weight (about 5 l.) from carefully dehydrated and fractionated absolute alcohol, and its density indicated a concentration by weight of 84·988%.

Measurements.—The thermostats could be set to 0·05°. The ester (0·1*M*) was weighed and made up to the appropriate volume at the thermostat temperatures. A few drops of 60% sodium hydroxide (to become 0·005*M*) were delivered from a micropipette into a dry flask in the thermostat and the ester solution was added and well shaken. Pipettes stored in a jacket in the thermostat were used to withdraw samples, which were run into aqueous hydrochloric acid and titrated, the acid solutions being kept at − 5° and subsequently warmed to the room temperature if they could not be titrated at once. As the measured concentration falls off with time substantially according to an exponential law under the conditions chosen, no error should arise through the finite time of delivery of the pipette (a simple calculation shows this), but the precaution was taken, nevertheless, to employ an especially rapid pipette for the faster reactions. The nozzle was widened to give delivery in 7 secs., and the top was provided with a 3-way tap, the extra branch of which contained a suitable air-leak; by means of this device the setting, which was observed from above with the use of an inclined mirror, could be done very rapidly. A 15-c.c. micro-burette was employed, which could be read to 0·01 c.c., although the end-point was estimated to be liable to an error of 0·05 c.c. The titrations, which were done in approximately 33% alcohol with bromothymol-blue as indicator, were facilitated in some cases by the addition of a little carbon tetrachloride to dissolve crystalline or viscous esters. Carbon dioxide-free reagents were used, and all end-points in a run were matched against the initial end-point, which for each run was matched against a permanent colour standard. It was verified that *p*-aminobenzoic acid, the weakest of the acids formed in the hydrolyses, could be accurately titrated.

Results.—Preliminary experiments (not recorded) were made to determine the best method of calculating the rate constants, and it was ultimately decided to use a modification of Guggenheim's method (*Phil. Mag.*, 1926, 2, 538), in which each result is used once only; in our modification each result is used once and given a weight proportional to its accuracy, *i.e.*, to the titre. Other preliminary experiments (below) showed that neutral-salt effects are small at the dilutions used.

Ethyl benzoate in " 50% " alcohol at 25·0°. Effect of neutral salts.

$[KOH]_{t=0}$ (= [KOH] + [KOBz])	0·005	0·005	0·010	0·010
[NaCl]	—	0·005	0·010	0·020
Total μ	0·005	0·010	0·020	0·030
$10^3 k_2$ (l./g.-mol./sec.)	1·30	1·32	1·32	1·32

A few experiments only were carried out in order to confirm the linearity of the usual logarithmic plot based on the Arrhenius equation, as this has previously been so very thoroughly established for ester hydrolysis in aqueous solution. The three following results fit the Arrhenius equation quite accurately.

Ethyl benzoate in 50% ethyl alcohol.

Temp.	25·0°	40·0°	50·0°
10^3k_2 (l./g.-mol./sec.)	1·33	9·32	20·00

The main series of results relate to " 85% " ethyl alcohol as solvent and the temperatures 25·0° and 50·0° (in one case 40°). The constants are summarised below. Those relating to the nitro-compound are less accurate than the others on account of the rapidity with which this ester undergoes hydrolysis.

p-*Substituted ethyl benzoates in* 85% *ethyl alcohol.*

(10^3k_2 in l./g.-mol./sec.)

p-Group	NH_2	OMe	Me	H	Cl	I	Br	NO_2
25·0°	0·0127	0·115	0·251	0·550	2·37	2·78	2·89	56·7
50·0°	0·172	1·31	2·71	5·56	21·3	24·8	25·9	183 *

* Temp. = 40·0°.

In the last table the rate constants are calculated relatively to those of the unsubstituted ester, and compared in this form with the figures derived by McCombie and Scarborough (J., 1915, **107**, 156) for hydrolysis in absolute ethyl alcohol at 30° and by Kindler (*Annalen*, 1926, **450**, 1) for hydrolysis in 87·83% (weight) aqueous ethyl alcohol at 30·0°.

Ratios (k_2^R/k_2^H) *of rate constants for* p-*substituted ethyl benzoates.*

p-Group (R)	NH_2	OMe	Me	[H]	Cl	I	Br	NO_2
Temp. 25°	0·0231	0·208	0·456	1·00	4·31	5·06	5·25	103·1
,, 50°	0·0308	0·232	0·480	1·00	3·78	4·39	4·57	—
McC. and S. (30°)	—	—	0·506	1·00	3·83	4·76	4·31	—
K. (30°)	0·0233	0·214	0·467	1·00	4·33	5·09	4·94	103·9

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50. *Mechanism of Substitution at a Saturated Carbon Atom. Part VI. Hydrolysis of* iso*Propyl Bromide.*

By Edward D. Hughes, Christopher K. Ingold, and Uriel G. Shapiro.

A recent publication (Taylor, J., 1935, 1514) opens with the following passage : " Hughes and Ingold (this vol., p. 246) have discussed the two types of mechanism—S_N1 and S_N2—for substitution by the nucleophilic hydroxyl ion at a saturated carbon atom. An entirely distinct mechanism is now brought forward to explain olefin formation when hydroxyl ion reacts with bromo- (and other halogeno-) ethanes." A detailed description of the mechanism follows this statement. As this mechanism (it is our E2) for the formation of olefins in hydrolysis was advanced by Hanhart and Ingold in 1927, and has since been discussed by Hughes or Ingold in eleven papers on 'onium ions, three on sulphones, and three on halogeno-paraffins, by von Braun in three papers on 'onium ions, and by Olivier in two papers on halogeno-paraffins, not to mention many references by other authors and a brief résumé in the *Annual Reports* for 1930, it would appear that the statement quoted obscures the history of the matter. Even Taylor's specific application of the mechanism (to the alternative olefin eliminations of polyhalogeno-compounds) was made, correctly and with adequate detail, by Olivier in 1934. Our general mechanisms are formulated for later reference; the numerical parts of the labels are reminders of the kinetic types to which the mechanisms belong :

$$\text{Y}\ \text{Alk—X} \longrightarrow \text{Y—Alk} + \text{X} \quad . \ . \ . \ . \ . \ . \ (\text{S}_\text{N}2)$$

$$\left.\begin{array}{l}\text{Alk—X} \longrightarrow \text{Alk}^+ + \text{X (slow)} \\ \text{Y}\ \text{Alk}^+ \longrightarrow \text{Y—Alk (fast)}\end{array}\right\} \quad . \ . \ . \ . \ (\text{S}_\text{N}1)$$

$$\text{Y}\ \text{H—C—C—X} \longrightarrow \text{YH} + \text{C=C} + \text{X} \quad . \ . \ . \ . \ . \ (\text{E}2)$$

We record below a kinetic study of the hydrolysis of *iso*propyl bromide, a key example as will appear, since the two substitutions S_N2 and S_N1 and the elimination E2 are all

present together, and can be shown to exhibit recognisably distinct kinetic characteristics. We here explain briefly the relation of this research to its predecessors.

In Part I (J., 1933, 526), Hughes, Ingold, and Patel discussed theoretically the nucleophilic substitution mechanisms S_N2 and S_N1 *inter alia*. They predicted (although there was then no kinetic evidence on the matter) that in a series Alk·X, such as

$$MeX, EtX, Pr^{\beta}X, Bu^{\gamma}X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (I)$$

in which Alk steadily increases in its power of electron release, S_N2 should prevail up to a certain point, after which S_N1 should take control; and that accordingly, before the transition point the substitution should exhibit second-order kinetics and an absolute rate decreasing with progression through the series, whilst after it, the kinetics should be first-order and the rate an increasing one. These and a number of other analogous predictions were verified in all detail when, in Part III (J., 1935, 236), Gleave, Hughes, and Ingold recorded the completion of a kinetic study of nucleophilic substitutions in structures of the form Alk·$\overset{+}{S}R_2$. For the reaction with hydroxide ions in water, for example, the mechanistic transition point in the above series was located between the ethyl and the *iso*propyl compounds. The next case to be considered was the analogous reaction of alkyl halides, to which, of course, the same predictions apply. In this field it was already known from the work of de Bruyn and Steger (*Rec. trav. chim.*, 1899, **18**, 41, 311) and Grant and Hinshelwood (J., 1933, 258) that methyl and ethyl halides undergo bimolecular reactions with alkali in alcohol or aqueous alcohol. Then Hughes showed in Part V (J., 1935, 255) that the hydrolysis of *tert.*-butyl chloride in aqueous alcohol or aqueous acetone is a reaction of the first order. This proved the presence of a mechanistic transition point somewhere in the alkyl series, but its location required the study of *iso*propyl halides.

With regard to the olefin elimination, E2, the most interesting question is whether it can be shown to be kinetically independent of the simultaneous substitution, as of course it must be if the mechanistic theories formulated above are correct. In the sulphonium ion series (I; X = $\overset{+}{S}R_2$), olefin elimination accompanies the hydrolysis of the ethyl, *iso*propyl, and *tert.*-butyl compounds. In the last case the substitution and elimination are obviously independent, since one is a reaction of the first order and the other one of the second. In the ethyl derivative, however, both the substitution and the elimination are second-order reactions. Possibly an experimental distinction could be drawn on the basis of the temperature coefficients of the rate constants, but this has not yet been done. In the alkyl halide series (I; X = Hal.), an appreciable olefin reaction accompanies hydrolytic substitution only in the cases of ethyl and *iso*propyl halides; and of these, only the ethyl compounds have previously been made the subject of kinetic measurements. Brussoff (*Z. physikal. Chem.*, 1900, **34**, 129) proved the occurrence of both reactions, and Grant and Hinshelwood (*loc. cit.*) measured the rate of the two together, but not of either separately. These authors considered the question of the possible kinetic independence of the two reactions, and showed that if they were independent this did not upset the fitting of the total rate constant to Arrhenius's equation. However, this is a hard test for independence, because unless both reactions are present in rather similar proportions (which according to both Brussoff and Grant and Hinshelwood is not the case), and unless also their (Arrhenius) energies of activation are well separated, the total rate constant would be likely to fit the equation anyhow.

As mentioned above, we have proved that the bimolecular and unimolecular substitutions and the bimolecular elimination are all present together in the hydrolysis of *iso*propyl bromide in aqueous alcohol. Further, we have measured the separate rate constants of the three reactions, studied the effect of solvent changes on each, and measured their separate temperature coefficients.*

* The circumstance that we can analyse the total substitution into components of different order is quite consistent with the view that no sharp line of demarcation exists between the two mechanisms, or, as Gleave, Hughes, and Ingold expressed it, that there are " *degrees* of collaboration " by the reagent in the work of removing the replaceable group (*loc. cit.*, p. 238).

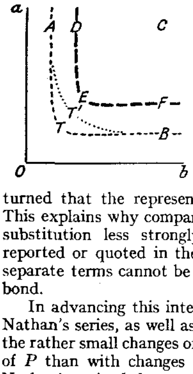
The method is as follows. A first-order reaction is isolated by the use of low concentrations of hydroxide ions, *i.e.*, by the employment of acidic or quite dilute alkaline solutions (cf. Hughes, *J. Amer. Chem. Soc.*, 1935, **57**, 708). No propylene is formed under these conditions, so that the reaction, measured by loss of alkalinity, increase of acidity, or liberation of bromide ions, must be the unimolecular substitution (S_N1) leading to *iso*propyl alcohol. At somewhat larger initial concentrations of hydroxide ions (*e.g.*, 0·1*N*) a " constant " calculated from the first-order formula falls during a run, and the fall becomes more marked the greater the initial alkalinity. This is due to the incursion of a second-order reaction. Correspondingly, the " constant " calculated from the second-order formula rises during a run, and the rise becomes less marked with each increase of the initial alkalinity. The previous determination of the true first-order constant enables us to calculate a true second-order constant. Concurrently with the incursion of the second-order process, propylene begins to appear amongst the products. A method has been developed by means of which the propylene can be accurately estimated by means of its reaction with bromine. It is found that the production of propylene accounts for only about half of the total second-order reaction, and is itself a second-order reaction (E2). The balance of the total second-order reaction represents the bimolecular substitution (S_N2) leading to *iso*propyl alcohol.*

Concerning the substitution process in the hydrolysis of alkyl halides, it will be apparent that the point at which the mechanism changes in the series Me, Et, Pr^{β}, Bu^{γ} has been located *at* the *iso*propyl group, for our solvents and concentrations. The comparison of absolute rates is not quite straightforward, but may be made as follows. De Bruyn and Steger (*loc. cit.*) studied the hydrolysis of methyl and ethyl iodides in a range of mixtures of ethyl alcohol and water, and it is clear from their results that the ethyl compound reacts more slowly. This is true even although the rate constants for ethyl iodide include the rate of olefin formation: for 80% ethyl alcohol as solvent, the ratio of the rates was 10 : 1, and this must be regarded as a conservative estimate of the ratio of the rates of the pure substitution processes. Grant and Hinshelwood (*loc. cit.*) measured the rate of hydrolysis of ethyl bromide in 100% ethyl alcohol, and we have studied the hydrolysis of *iso*propyl bromide in 60% and 80% ethyl alcohol but not in pure alcohol. As the measurements stand, the *iso*propyl halide reacts the more slowly, the ratio of Grant and Hinshelwood's rate in pure alcohol to our second-order rate (for the substitution alone) in 80% alcohol being 46 : 1. This ratio needs correction, however, first because the rate for ethyl bromide includes the rate of olefin formation, and secondly because the solvents differ. (In the latter connexion we have to consider, not only the environmental influence of the solvent, but also the circumstance that the reaction leading to an ether could not have been a negligible constituent of Grant and Hinshelwood's measured rate.) The first correction will reduce the ratio, but not by much, since Grant and Hinshelwood state that the proportion of olefin formed is small. The second correction will also reduce the ratio, but again by a rather small factor, the order of magnitude of which can be estimated from various results, *viz.*, de Bruyn's, Hinshelwood's, Taylor's, and our own. Taking everything into account, it would appear that the real ratio must lie in the neighbourhood of 25 : 1. Thus there is continuous diminution in the series, Me, Et, Pr^{β}, with regard

* Two solvents were employed, *viz.*, 60% and 80% aqueous ethyl alcohol. In the latter solvent, 20—30% of the product of the unimolecular substitution (S_N1) is actually ethyl *iso*propyl ether. However, the alcohol in the solvent intervenes only in the fast stage of this reaction, and the only concentration entering explicitly into the velocity equation is that of *iso*propyl bromide. In the same 80% alcoholic solvent, about 2% of the total bimolecular reaction (S_N2 + E2) results in the formation of the ether, and this means that about 5% of the bimolecular substitution (S_N2) represents replacement of the halogen by OEt, and 95% replacement by OH. Here the measured rate involves the concentration of the attacking anion, which in the text is taken as OH^-, the fact that a little of it is really OEt^- being disregarded for the sake of simplicity. This is justified because the effect of the minor reaction on the determinations of critical energy would be inappreciable, provided that, as is extremely probable, the critical energies of the reactions of the two anions do not differ by more than 2 or 3 kg.-cals. For the other solvent, 60% alcohol, the proportions in which ether is formed are smaller, and, in the case of the bimolecular reaction, barely appreciable.

to the second-order rates. The first-order rate constants for *iso*propyl bromide (this paper) and *tert.*-butyl chloride (Hughes, *loc. cit.*) in 80% alcohol at 45° stand in the ratio 1 : 134, and it is known qualitatively that *tert.*-butyl bromide is hydrolysed considerably more rapidly than the chloride. Thus there is a very marked increase from Pr^{β} to Bu^{γ}, with respect to first-order rates. These are just the predicted effects.

When previously discussing such relations, Hughes and Ingold foresaw the possibility that in some series, ascending in the electron release of the alkyl substituent, the change from a decreasing to an increasing rate might occur at an earlier point than the change from second- to first-order kinetics; but they could not find a clear example. Since then, Baker and Nathan have produced one in their study of the reaction between substituted benzyl bromides and pyridine (J., 1935, 1840). Accordingly, we may set forth this feature in the theory more fully than heretofore. We know that in a bimolecular reaction the associative and dissociative processes cannot be given separate energies, and yet it has to be shown why we might expect a progressively increasing electron accession to the reaction zone to act in the early stages as though it was principally occupied in repelling the reagent and (perhaps) at a later stage as though it were mainly engaged in expelling the replaceable group (even though the reaction is still bimolecular). The situation is most easily understood with the aid of an imaginary potential surface (see fig.), which we assume to possess not only the two valleys A and B usual for a gas reaction with a transition state at T but also a third valley at C (due to ion solvation) together with the included pair of ridges DEF. With increasing electron accession to the reaction zone we expect an increasing gradient, negative in directions Oa and Ob, to be imposed on the original surface. The first effect of this will be to raise the energy of the activation AT, the reaction track ATB undergoing originally only a very slight displacement away from the origin. At a later stage, however, when the increasing tilt has depressed the ridges DEF and largely flattened the hill TE, the reaction track $AT'B$ will fan out much more widely. This would lead to a reduced increase, and possibly an actual decrease, in the activation energy, and in certain cases the decrease might set in before the reaction track has become so far turned that the representative point runs over into valley C (unimolecular reaction).



This explains why comparable structural changes always affect the rate of a bimolecular substitution less strongly than that of the allied unimolecular reaction (examples reported or quoted in these papers): the former effect is a difference, even although the separate terms cannot be associated each exclusively with the formation or rupture of a bond.

In advancing this interpretation, we are not perturbed by the fact that in Baker and Nathan's series, as well as in a number of others where no rate minimum has been found, the rather small changes of rate with structure are found to be correlated more with changes of P than with changes of E when the equation $k = PZe^{-E/RT}$ is applied. Baker and Nathan's series belongs to the important group of those which avoid local effects due to substitution very close to the site of reaction; and within this group it is the rule that large changes of absolute rate are correlated essentially with changes of E—exactly as the electronic theory of reaction mechanism requires that the changes of rate should be correlated with changes of the critical energy (preceding paper). Now a critical energy which theory treats as a structural constant is evidently not to be identified *exactly* with the Arrhenius critical energy, E, which, like P, is a function of temperature. An apparent straightness in the usual logarithmic plot over perhaps a 10—15% range of T does not furnish a good reason for disregarding this distinction, since an inappreciable difference of slope between two halves of such a plot could easily correspond to a considerable difference between the mean slope and its limit $T \longrightarrow 0$.* This does not mean that it is useless to examine the dependence of changes of rate with structure and solvent on changes in the

* *A new experimental demonstration of the temperature dependence of the Arrhenius critical energy has been published by La Mer and Miller (J. Amer. Chem. Soc., 1935, 57, 2674).*

Arrhenius parameters; but it does mean that the results should be interpreted with reserve unless the differences are large.

To avoid misconception it may be added that we recognise the existence of structural series in which large changes of the rate are correlated largely with changes of P; however, the circumstances in which this can happen seem to be fairly clear. Structural series may be divided into two chief classes according to whether local effects are absent or present. If they are absent, a further sub-division is possible according to whether or not the effect of the distant substituent can be carried by an electrically conducting (unsaturated) system the whole of the way to the site of reaction. If it can, then the changes of rate may be large, and if so they will be correlated essentially with changes of E (examples: *aroylation of arylamines; hydrolysis of benzoic esters*, see preceding paper). However, as we have seen, there are bimolecular reactions sufficiently near to the border region between bimolecular and unimolecular mechanisms to exhibit a marked reduction or even an inversion of the normal critical energy differences, so that a simple relation between rate and the Arrhenius energy E is not always to be expected. If an electrically conducting system does not extend from the distant substituent to the reaction zone, then in any case the changes of rate will be relatively small and their relation to E more or less obscured (*e.g.*, halogen exchange in β-arylthioethyl chlorides; Baddeley and Bennett, J., 1933, 261). The remaining alternative is that local effects are present. In this case the general result is that both P and E are changed, possibly quite largely, P because local substitution must seriously affect the entropy of the transition state (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1934, **31**, 875), and E because, even in a non-conducting (saturated) system, the variable group will in general be near enough to the reaction zone to affect the energy of the transition complex through dipolar, dispersion, or steric repulsive forces (*e.g.*, esterification, quaternary ammonium salt formation; Hinshelwood, Winkler and Legard, J., 1934, 1079; 1935, 587, 1147, 1588). These forces are mentioned in order of decreasing range, and it can readily be understood how, in particular cases, a substituent situated just beyond the distance from which it can largely influence the energy of activation may yet affect its entropy considerably.

The temperature coefficients of the three simultaneous reactions occurring in the hydrolysis of *iso*propyl bromide are distinct though not at all widely different. In "60%" aqueous alcohol E for the unimolecular substitution is 22,690 cals. For the bimolecular substitution it is 20,760 cals., and for the bimolecular elimination 22,100 cals. In spite of the difference of 1340 cals. between their energies, the two bimolecular rates when added together give a sum which fits the Arrhenius equation very well.

Comparison of the results obtained with "60%" and "80%" ethyl alcohol as solvent shows that the addition of water to the alcoholic medium rather strongly accelerates the unimolecular reaction, slightly retards the bimolecular substitution, and somewhat more strongly retards the elimination. All these effects agree with, and could have been predicted from, Hughes and Ingold's theory of solvent action (J., 1935, 252). An analysis in terms of the factors of the Arrhenius equation is given but the differences are rather small and quite irregular. In a discussion which disregards the uncertainties attaching to the interpretation of the Arrhenius parameters, Taylor (*loc. cit.*) has complained that the solvent theory neglects the non-exponential rate factor. Actually, of course, this factor is recognised, but an analysis involving its separate treatment is precluded by the absence at the present time of a tractable theoretical method, even for reactions in the gaseous phase (cf. J., 1935, 246). It may be noted that, since both the temperature coefficient and the retarding effect of water are greater for the olefin reaction than for substitution, and since a high concentration suppresses the unimolecular substitution, the best yields of olefin will be obtained by avoiding water and using a high concentration and temperature—just the conditions which, to judge from preparative recipes ("hot strong alcoholic potash"), have long since been considered the most appropriate for the production of olefins generally. The rate constants are summarised in Tables X and XI.

EXPERIMENTAL.

Materials.—The *iso*propyl bromide was dried with anhydrous sodium carbonate and calcium chloride and fractionated, the fraction, b. p. 60°/760 mm., being used for the measurements. Commercial absolute alcohol was dried over lime and fractionated. The "60%" aqueous alcohol was made by mixing 6 l. of this absolute alcohol with 4 l. of water, and the "80%" aqueous alcohol by mixing 8 l. of the alcohol with 2 l. of water.

Rate Measurements.—The thermostats could be set to within 0·05°. The usual initial concentration of *iso*propyl bromide was $N/10$. The reaction mixture was enclosed in the cold in portions of 5 c.c. in sealed tubes, which were placed in the thermostat for known times, and then broken under 100 c.c. of absolute alcohol. Two methods of estimation were used. In the first the acid or alkali was titrated with, *e.g.*, 0·02N-sodium hydroxide (carbonate-free) or hydrochloric acid, lacmoid being used as indicator (phenolphthalein is inapplicable in the presence of much alcohol). In the second method, bromide ion was estimated in the neutralised or faintly acidic solution by titration with, *e.g.*, 0·01N-silver nitrate in the presence of eosin (adsorption indicator). For acidic or dilute alkaline solutions ($<$ 0·1N-alkali) either method may be used, and usually both were employed with concordant results, the second being applied to the solution obtained after completion of the first. For more strongly alkaline solutions the first method is less accurate, and the estimations were made by the second method.

Estimation of Propylene.—The sealed tube enclosing 5 c.c. of the reaction mixture containing the propylene to be estimated was broken by shaking under water, containing enough sulphuric acid to neutralise the alkali, in an evacuated stoppered jar provided with an inlet and an outlet tube, the former reaching to the bottom. By means of a slow stream of nitrogen, the propylene was swept through a trap at − 5° and through two bubbling tubes containing known quantities of a standard solution of bromine in chloroform. The second tube was kept at 0°, and a trap containing aqueous potassium iodide was placed at the end of the gas train. The jar being kept at 50—60°, the whole of the propylene could be swept over in ¾ hour and estimated by titrating the remaining bromine with standard thiosulphate.

The First-order Reaction.—A reaction was started in dilute alkaline solution ($N/200$) in "60%" alcohol and followed by titration with standard acid until the original alkali had disappeared. A good first-order constant was obtained. The experiment was then continued, and the development of free acid followed by titration with standard alkali. A good first-order constant was again obtained. The two first-order constants agreed to within 1% (Table I). For further kinetic investigation of the first-order reactions, initially neutral solutions were used for convenience. The rate was measured in the two solvents "60%" and "80%" aqueous alcohol, and at four temperatures (Tables II and III). It was shown that increasing the concentration of *iso*propyl bromide from the usual $M/10$ to $M/5$, and adding sodium bromide ($M/7$) initially, had only very small effects on the rate. Some of these experiments were done by the method of pipetting the samples and others by the sealed-tube method; but since in each case the initial concentration of *iso*propyl bromide was estimated for the calculation of the constants by an analysis made in the same way after completion of the reaction, it follows that the constants are unaffected by the deviations of concentration arising from the rather considerable thermal expansion of alcohol. It was proved that no propylene is formed under the conditions of the experiments.

The Total Second-order Reaction.—In $N/50$-alkaline solution the first-order constant shows a just perceptible drift throughout the reaction. The drift, a descent with increasing time, becomes more marked in stronger solutions until, in $N/5$-alkali, the first-order formula is quite inapplicable. On the other hand, the second-order formula is inapplicable in $N/50$-alkali, the "constant" rising rapidly during a run; but in more concentrated alkali the rise becomes less marked until in N-alkali it has become inappreciable. These observations led to the assumption that first- and second-order reactions are present together (Table IV). Assuming that the presence of the sodium hydroxide does not cause any marked change in the first-order velocity, the determined value for this may be used to calculate the second-order constant by a method described later. This was done for the "60%" alcoholic solvent and initial concentrations of sodium hydroxide ranging from $N/10$ to N, and it was found that the second-order constant fell by about 40% over this range (Table VII). It is believed that this effect is due to the ionic strengths of the solutions, since the application in the calculations of the activity coefficients of sodium hydroxide in water (the activities in 60% ethyl alcohol being unknown) brings the constants much closer together. The main series of determinations of the second-order constant were carried out in N-alkaline solution in order that the measurement should be as direct as

possible; at this concentration over 90% of the whole reaction is of the second order. Measurements were made in " 60% " and in " 80% " alcohol, in the former solvent at three temperatures and in the latter at two (Tables V and VI). These determinations were all made by the method of separate sealed tubes and are therefore subject to an error due to thermal expansion of the solvent: the concentrations used in the evaluation of the reactiou rate are based on a measurement of volume made at room temperature and are therefore greater than the actual concentrations obtaining during reaction at higher temperatures. Since second-order rate constants involve the reciprocal of a concentration it follows that they must be affected, even though the initial concentrations of reactants were determined from an analysis made after the completion of reaction. The error, which is probably just outside the limits of consistency of the observations, is not appreciably greater in " 80% " aqueous alcohol than in " 60%."

The Olefin Elimination.—From the determined values of the first- and second-order rate constants it is possible to calculate what proportion of the total reaction which has occurred at any time (or at infinite time) is of the second order. It is also possible to estimate the amount of olefin formed by the method described above. It was found that this only accounts for a part of the total second-order reaction. The olefin reaction was shown to be of the second order by the demonstration (*a*) that the amount of olefin formed at various times during a run is a constant fraction of the total second-order reaction taking place in the same times, and (*b*) that the amount of olefin formed on completion of different runs with different initial concentrations of alkali is a constant fraction of the total second-order reaction occurring in these runs. Both ratios were constant to within 1% (Table VIII). Having demonstrated this, it was necessary only to measure the olefin formed on completion of any run with a solvent and temperature for which the first- and second-order rate constants were known in order to find the ratio in which the second-order rate constant should be split up between the second-order substitution and the elimination. This was done for " 60% " alcohol at four, and for " 80% " alcohol at three temperatures (Table IX).

Calculation of the Total Second-order Rate Constant.—The problem is to calculate the second-order constant, given the first, from observations of the total reaction. The formula used, which is very convenient, is easily derived for the general case of two reactions, of order m and n, which may be either simultaneous or opposing. In either case let the reaction rate be governed by the equation

$$dx/dt = k_m f_m(x) + k_n f_n(x)$$

where f_m and f_n are the appropriate functions of concentration. Define a quantity $\mathbf{k}_n$ by the relation

$$\mathbf{k}_n = \frac{1}{t}\int_0^x \frac{dx}{f_n(x)} = \frac{1}{t}\cdot J$$

where J is simply an abbreviation for the definite integral. This amounts to applying to the whole reaction the integrated velocity equation of its nth order constituent; the " constant " thus obtained is not the true constant k_n, or even a constant at all, but is a function of x and therefore of t. By plotting it against t we can find the value, for any t, of the expression $t(d\mathbf{k}_n/dt)$. Then we have

$$\mathbf{k}_n + t\frac{d\mathbf{k}_n}{dt} = \frac{dJ}{dt} = \frac{dJ}{dx}\cdot\frac{dx}{dt} = \frac{1}{f_n(x)}\cdot\frac{dx}{dt} = k_m\frac{f_m(x)}{f_n(x)} + k_n$$

If k_m is known, k_n can be obtained at once, and if k_m is not known both k_m and k_n can be calculated by cyclic approximation, using the same formula with repeatedly interchanged subscripts. In our case we define $\mathbf{k}_2$ by the equation

$$\mathbf{k}_2 = \frac{1}{t(b-a)}\cdot\log_e\frac{b(a-x)}{a(b-x)}\quad\left[\text{or } \mathbf{k}_2 = \frac{1}{ta}\cdot\frac{x}{a-x} \text{ in case } a = b\right]$$

and calculate k_2 from

$$k_2 = \mathbf{k}_2 - \frac{k_1}{b-x} + t\cdot\frac{d\mathbf{k}_2}{dt}$$

The equation is exact, but the three terms on the right-hand side are of successively decreasing importance so long as most of the reaction is of the second order, and indeed in these circumstances the last term is often negligible.

Calculation of Separate Second-order Rate Constants.—In order to be able to split up k_2 into its two constituents, it is necessary to calculate the proportion $x_1/(x_1 + x_2)$ in which a reaction $x = x_1 + x_2$ has proceeded through the unimolecular route. For this purpose we decompose the equation

$$dx/dt = k_1(a - x) + k_2(a - x)(b - x)$$

into its two constituents,

$$dx_1/dt = k_1(a - x_1 - x_2)$$
$$dx_2/dt = k_2(a - x_1 - x_2)(b - x_1 - x_2),$$

divide the second by the first

$$dx_2/dx_1 = (k_2/k_1)(b - x_1 - x_2)$$

and integrate, using the condition $x_2 = 0$ when $x_1 = 0$ in order to evaluate the constant of integration. The result is

$$x_1 = (k_1/k_2)\log_e[\{(k_1/k_2) + b\}/\{(k_1/k_2) + b - x\}],$$

and the approximation

$$x_1/(x_1 + x_2) = x_1/x = k_1/\{k_1 + k_2(b - \tfrac{1}{2}x)\}$$

may be used when x is small.

Results for the First-order Rate Constants.—Tables I, II, and III relate to first-order rate constants (reaction S_N1) calculated from the formula $k_1 = (1/t)\log_e\{a/(a - x)\}$, where a is the initial concentration of *iso*propyl bromide and x the decrease of concentration; a was determined by measuring the asymptotic value of x at large times. Table I illustrates an experiment showing that the first-order rate constant is the same in a dilute alkaline as in an acid medium. Table II is an illustrative record of one of a set of 16 determinations of the rate of the unimolecular reaction in different solvents at different temperatures. Table III records the constants obtained in this set of measurements. In general, the initial concentration of *iso*propyl bromide was about $N/10$ in this series, and nothing else was added to the aqueous-alcoholic medium at the commencement of reaction. Expt. 13, however, shows the small medium effect obtained by increasing the initial concentration to $N/5$, and Expt. 14 illustrates the effect of adding sodium bromide initially in a concentration of $N/7$, the concentration of *iso*propyl bromide being once again the usual $N/10$. These two experiments are excluded in deriving the mean values of the rate constants (summarised later).

Table I.

Expt. 1. Comparison of rate in dilute alkaline and acid solution. Solvent: "60%" aqueous alcohol. Temp. 45·0°. Constants, k_1, in hours^{-1}.

Alkaline solution.

Initially: $[Pr^{\beta}Br] \sim N/5$; NaOH = $N/200$. Samples of 10 c.c. titrated. $[Pr^{\beta}Br]$ in c.c. of 0·986 × $N/200$-HCl.

t (hrs.).	$[Pr^{\beta}Br]$.	10^3k_1.
0·00	425·80	—
1·10	422·10	7·95
2·20	419·05	8·04
2·50	417·35	7·93
		Mean: 7·97

Acid solution.

Initially: $[Pr^{\beta}Br] \sim N/5$; NaOH = 0. Samples of 10 c.c. titrated. $[Pr^{\beta}Br]$ in c.c. of 1·270 × $N/200$-NaOH.

t (hrs.).	$[Pr^{\beta}Br]$.	10^3k_1.
0·00	321·80	—
1·00	319·30	7·83
2·25	316·55	7·37
3·25	314·30	8·49
		Mean: 7·90

Table II.

Expt. 16. Illustrating determination of unimolecular rate constant. Solvent: "60%" aqueous alcohol. Temp. 65·0°. Initially $[Pr^{\beta}Br] \sim N/10$ and [NaOH] = 0. Samples of 5 c.c. titrated. $[Pr^{\beta}Br]' = [Pr^{\beta}Br]$ as determined in c.c. of 1·109 × $N/50$-NaOH; k_1' = corresponding k_1 in hours^{-1}. $[Pr^{\beta}Br]'' = [Pr^{\beta}Br]$ as determined in c.c. of $N/100$-$AgNO_3$; k_1'' = corresponding k_1 in hours^{-1}.

t (hrs.).	$[Pr^{\beta}Br]'$.	$[Pr^{\beta}Br]''$.	$10^2k_1'$.	$10^2k_1''$.	t (hrs.).	$[Pr^{\beta}Br]'$.	$[Pr^{\beta}Br]''$.	$10^2k_1'$.	$10^2k_1''$.
0·00	22·50	49·90	—	—	8·50	13·00	28·60	6·52	6·54
2·10	19·50	43·20	6·82	6·82	9·90	11·50	25·35	6·79	6·84
3·25	18·05	39·75	6·79	6·68	12·00	10·00	22·00	6·75	6·81
4·25	16·85	37·25	6·82	6·88	24·00	4·65	10·00	6·56	6·70
5·50	15·45	34·35	6·82	6·79	31·00	2·65	5·60	6·91	—
7·00	14·10	30·95	6·68	6·82			Means	6·75	6·76

TABLE III.

Expts. 11—26. Summary of first-order rate constants. Initially: $[Pr^{\beta}Br] \sim N/10$, $[NaOH] = 0$, and $[NaBr] = 0$ except in Expts. 13 and 14. k_1' and k_1'' are rate constants in $hours^{-1}$ as determined by titration with NaOH and $AgNO_3$ respectively.

Solvent: "60%" aqueous alcohol.				*Solvent: "80%" aqueous alcohol.*			
Expt.	Temp.	$10^2k_1'$.	$10^2k_1''$.	Expt.	Temp.	$10^2k_1'$.	$10^2k_1''$.
11	45·0°	0·798	0·804	20	45·0°	—	0·278
12	,,	0·798	—	21	,,	0·276	0·276
13 *	,,	0·745	—	22	55·0	0·844	0·856
14 †	,,	0·750	—	23	65·0	2·44	2·47
15	55·0	2·39	2·40	24	,,	2·42	2·42
16	65·0	6·75	6·76	25	75·0	6·59	6·50
17	,,	6·74	—	26	,,	6·55	6·56
18	75·0	17·5	17·6				
19	,,	17·9	17·7				

* Initial $[Pr^{\beta}Br] = N/5$.
† ,, $[NaBr] = N/7$.

Results for the Total Second-order Rate Constants.—Tables IV—VII relate to the total second-order rate constants (reactions $S_N2 + E2$) as calculated from the formula

$$k_2 = \{1/t(b-a)\} \log_e\{b(a-x)/a(b-x)\}, \text{ or } k_2 = x/ta(a-x) \text{ if } a = b,$$

after modification to allow for the simultaneous unimolecular reaction (above). Here b is the initial concentration of sodium hydroxide; a and x have already been defined. Table IV(A) illustrates the constancy of $\mathbf{k}_1$ and the drift of $\mathbf{k}_2$ when these "constants" are calculated by applying to the whole reaction in $N/50$-sodium hydroxide the integrated rate equations without correction for the fact that first- and second-order reactions are present together; $\mathbf{k}_1$ is nearly constant in this case because the proportion of second-order reaction is small. Table IV(B) shows the effect obtained when the same uncorrected equations are applied to the reaction in $N/10$-sodium hydroxide: here the proportion of the first-order reaction is small. In judging the drifts of the "constants" it must be borne in mind that in the first case only about 8% of the total amount of *iso*propyl bromide is consumed during the run, and in the second about 50%. Table V is an illustrative record of one of a set of 12 determinations of the true bimolecular rate constant for different solvents and temperatures. Table VI summarises the constants obtained in this series of experiments. Expt. 45 was a closely concordant duplicate of the initial part of Expt. 44, but is not recorded because it could not be completed owing to thermostat trouble. Table VII shows the effect of the concentration of sodium hydroxide on the bimolecular rate constants. The value obtained with an initial $N/10$-concentration of alkali is only approximate. Throughout all the experiments recorded in Tables IV—VII the initial concentration of *iso*propyl bromide was about $N/10$, and in the experiments of Table VI, the initial concentration of sodium hydroxide was about $0{\cdot}85N$; this rather high value was chosen in order that the reaction whose rate was sought should be the principal one, and it was maintained roughly constant throughout the series in order to standardise the activity effects to which the variations of rate exhibited in Table VII are ascribed.

TABLE IV.

Expts. 31, 32. Application of integrated rate equations to reaction in $N/50$- and $N/10$-sodium hydroxide. Solvent: "60%" aqueous alcohol. Temp. 45·0°. Initially $[Pr^{\beta}Br] \sim N/10$. Samples of 5 c.c. titrated. $[Pr^{\beta}Br]$ and [NaOH] expressed as equivalent c.c. of $N/200$-$AgNO_3$. $\mathbf{k}_1$ in $hours^{-1}$; $\mathbf{k}_2$ in l./g.-mol./hour.

(A) Initial [NaOH] $\sim N/50$.					(B) Initial [NaOH] $\sim N/10$.				
t (hrs.).	$[Pr^{\beta}Br]$.	[NaOH].	$10^3\mathbf{k}_1$.	$\mathbf{k}_2$.	t (hrs.).	$[Pr^{\beta}Br]$.	[NaOH].	$10^3\mathbf{k}_1$.	$10\mathbf{k}_2$.
0·00	100·00	21·50	—	—	0·00	88·40	88·40	—	—
1·00	98·75	20·25	1·27	2·18	3·00	81·10	81·10	2·88	3·00
2·02	97·50	19·00	1·26	2·26	5·00	76·80	76·80	2·81	3·02
3·00	96·30	17·80	1·26	2·35	7·00	72·60	72·60	2·81	3·11
4·00	95·20	16·70	1·23	2·37	11·50	65·60	65·60	2·60	3·02
6·50	92·50	14·00	1·20	2·51	16·75	58·50	58·50	2·49	3·05
7·25	91·70	13·20	1·20	2·57	22·00	52·50	52·50	2·37	3·11
					26·00	48·70	48·70	2·30	3·14
					31·50	44·20	44·20	2·19	3·17

TABLE V.

Expt. 44. Illustrating determination of bimolecular rate constant. Solvent: "80%" aqueous alcohol. Temp. 50·0°. Initially [$Pr^{\beta}Br$] ~ $N/10$; [NaOH] ~ 0·8N. Samples of 5 c.c. titrated. [$Pr^{\beta}Br$] and [NaOH] expressed in c.c. of $N/100$-silver nitrate. $\mathbf{k}_2$ is the uncorrected bimolecular "constant" in l./g.-mol./hour. "Corr. k_1" signifies the correction to be applied to $\mathbf{k}_2$ in order to allow for the unimolecular reaction. k_2 is the corrected constant in l./g.-mol./hour.

t (hrs.).	[$Pr^{\beta}Br$].	[NaOH].	$\mathbf{k}_2$.	"Corr. k_1."	k_2.
0·00	46·00	399·00	—	—	—
0·35	43·20	396·20	0·226	0·006	(0·220)
1·00	37·70	390·70	0·252	0·006	0·246
1·50	34·35	387·35	0·248	0·006	0·242
2·25	29·70	382·70	0·249	0·006	0·243
3·10	25·60	378·60	0·244	0·006	0·238
4·00	21·60	374·60	0·245	0·006	0·239
5·05	17·80	370·80	0·246	0·007	0·239
6·05	14·40	367·40	0·253	0·007	0·246
8·50	9·70	362·70	0·243	0·007	0·236
					Mean: 0·241

TABLE VI.

Expts. 36—47. Summary of bimolecular rate constants. Initially [$Pr^{\beta}Br$] ~ $N/10$ and [NaOH] ~ 0·85N. k_2 *is in l./g.-mol./hour.*

Solvent: "60%" aqueous alcohol.						*Solvent: "80%" aqueous alcohol.*		
Expt.	Temp.	k_2.	Expt.	Temp.	k_2.	Expt.	Temp.	k_2.
36	45·0°	0·1060	40	60·0°	0·485	44	50·0°	0·241
37	,,	0·1068	41	,,	0·490	46	80·0	4·64
38	60·0	0·483	42	,,	0·488	47	,,	4·57
39	,,	0·487	43	75·0	2·000			

TABLE VII.

Expts. 41—44. Variation of bimolecular rate constant with initial [NaOH]. Solvent: "60%" aqueous alcohol. Temp. 45·0°. Initial [$Pr^{\beta}Br$] ~ $N/10$.

Initial [NaOH], g.-mol./l.	0·1	0·2	0·5	1·0
k_2, l./g.-mol./hr.	0·183	0·169	0·134	0·106

Results for the Ratio of the Separate Second-order Rates.—Table VIII exemplifies results establishing the point that the olefin elimination is a bimolecular reaction, because the amount of olefin formed is a constant fraction of the total bimolecular reaction, independently of the time during a run or of the initial concentrations of alkali in different runs. The table shows in successive columns the initial concentration of alkali, the proportion of the total possible reaction which had actually occurred when the sample was taken for the estimation of olefin, and the extents to which the various constituent reactions have taken place at the same time, these quantities being in every case expressed as percentages of the total actual reaction at the time in question. The figures in col. 3 are derived by calculation from the first- and second-order constants, using the formulæ given above; those in col. 4 follow by difference. The data in col. 5 are observations of the yield of olefin; those in col. 6 follow by difference. Cols. 7 and 8 show the fractions in which the total actual bimolecular reaction is partitioned between the substitution and olefin elimination. Their constancy shows that they represent the ratios in which the total second-order rate constants have to be split up to give the rate constants for the bimolecular substitution and the elimination. It is also clear that in order to obtain these ratios it is not necessary to estimate olefin at various times throughout the progress of reaction: estimations made with the product of the completed reaction should suffice if the first- and second-order rate constants are known. Utilising this result, a series of experiments were made to determine the percentage of olefin formed in the completed reaction in various solvents and at various temperatures: the data obtained are in Table IX. Col. 4 gives the observed percentages, each of which represents the mean of four observations, of propylene, col. 5 the calculated percentage of products formed by the unimolecular reaction, and col. 6 the figures, obtained by difference, for the products formed by the bimolecular reaction. The last two cols. contain the factors which, when multiplied into the total second-order rate constants, will give the rate constants for the two separate bimolecular reactions.

TABLE VIII.

Expts. 51—54. Constancy of the ratio of olefin formed to the total second-order reaction. Solvent : "60%" aqueous alcohol. Temp. 60°. Initial [Pr^βBr] ~ $N/10$.

Initial [NaOH].	Actual/possible reaction.	S_N1 (%). (calc.).	S_N2 + E2 (%) (total 2nd order).	E2 (%) (obs.).	S_N2 (%) (diff.).	$\frac{S_N2}{S_N2 + E2}$.	$\frac{E2}{S_N2 + E2}$.
0·940	0·373	8·25	91·75	50·0	41·75	0·455	0·545
,,	0·607	8·35	91·65	49·9	41·75	0·456	0·544
,,	1·000	8·40	91·6	50·9	40·7	0·444	0·556
0·465	1·000	14·50	85·5	47·9	37·6	0·440	0·560

TABLE IX.

Expts. 61—67. Proportion of olefin formed in completed reactions. Initial [Pr^βBr] ~ $N/10$. Initial [NaOH] ~ $0·85N$.

Expt. No.	Solvent.	Temp.	E2 (%) (obs.).	S_N1 (%) (calc.).	S_N2 (%) (diff.).	$\frac{S_N2}{S_N2 + E2}$.	$\frac{E2}{S_N2 + E2}$.
61	"60%" aqueous alcohol	45·0°	48·73	8·38	42·89	0·468	0·532
62		60·0	50·78	8·92	40·30	0·443	0·557
63		75·0	52·45	9·03	38·52	0·424	0·575
64		100 *	56·85	10·68 †	32·47	0·364	0·636
65	"80%" aqueous alcohol	50·0	56·76	2·59	40·65	0·419	0·581
66		80·0	59·40	2·90	37·70	0·388	0·612
67		100 *	64·46	3·15 †	32·30	0·335	0·665

* Temperature maintained by boiling water-bath only, and not accurately controlled.

† As k_1 and k_2 were not measured for this temperature, the values necessary for the calculation were obtained by extrapolation using the Arrhenius formula.

Mean Values and Temperature Coefficients of Rate Constants.—Table X(*a*) shows the mean values of the unimolecular rate constants, k_1 (reaction S_N1), for the solvents and temperatures investigated, together with energies of activation calculated from the formula $k_1 = Be^{-E/RT}$; k_1 and B are in hours^{-1} and E in cals. Table X(*b*) contains similar data relating to the total bimolecular rate constants, k_2 (reactions S_N2 + E2), the energies of activation being calculated from the formula $k_2 = Be^{-E/RT}$; k_2 and B are in l./g.-mol./hour. Table X(*c*) refers to the bimolecular substitution (reaction S_N2); the rate constants, k_2, are obtained by decomposing the bimolecular rate constants of Table X(*b*) in accordance with the factors given in Table IX. Table X(*d*) exhibits similarly obtained rate constants, k_2, for the elimination (reaction E2). In Tables X(*c*) and X(*d*) the temperature coefficients are expressed as Arrhenius critical energies calculated from equations of the form given above. In Table XI we summarise the formulæ expressing the rate constants of the several reactions, and in order to facilitate comparison we give also the calculated rate constants for 50°.

TABLE X.

(*a*) *Reaction* S_N1.

Rate constants.			Temp. coeff.		
Temp.	"60%" EtOH. k_1.	"80%" EtOH. k_1.	Temps.	"60%" EtOH. E.	"80%" EtOH. E.
45·0°	0·00800	0·00277	45—55°	22,750	23,210
55·0	0·0240	0·00850	55—65	22,760	23,130
65·0	0·0675	0·0244	65—75	22,520	23,160
75·0	0·0177	0·0655	45—65	22,760	23,160
			55—75	22,650	23,140
			45—75	22,690	23,170

(*b*) *Reactions* S_N2 + E2.

Rate constants.			Temp. coeff.		
Temp.	"60%" EtOH. k_2.	"80%" EtOH. k_2.	Temps.	"60%" EtOH. E.	"80%" EtOH. E.
45·0°	0·1064	—	45—60°	21,300	—
50·0	—	0·241	60—75	21,670	—
60·0	0·487	—	45—75	21,490	—
75·0	2·000	—	50—80	—	22,250
80·0	—	4·600			

(*c*) *Reaction* S_N2.

Rate constants.			Temp. coeff.		
Temp.	k_2.	k_2.	Temps.	E.	E.
45·0°	0·0498	—	45—60°	20,560	—
50·0	—	0·101	60—75	20,960	—
60·0	0·216	—	45—75	20,760	—
75·0	0·849	—	50—80	—	21,700
80·0	—	1·79			

(*d*) *Reaction* E2.

Rate constants.			Temp. coeff.		
Temp.	k_2.	k_2.	Temps.	E.	E.
45·0°	0·0566	—	45—60°	21,950	—
50·0	—	0·140	60—75	22,250	—
60·0	0·271	—	45—75	22,100	—
75·0	1·153	—	50—80	—	22,640
80·0	—	2·81			

TABLE XI.

Summary of formulæ expressing rate constants.

(k_1 in hours; k_2 in l./g.-mol./hour.)

Reaction.	" 60% " Aqueous alcohol.	" 80% " Aqueous alcohol.
S_N1	$\log_e k_1 = 31 \cdot 18 - 22{,}690/RT$ $k_1^{50°} = 0 \cdot 0148$	$\log_e k_1 = 30 \cdot 79 - 23{,}160/RT$ $k_1^{50°} = 0 \cdot 00482$
S_N2	$\log_e k_2 = 29 \cdot 88 - 20{,}760/RT$ $k_2^{50°} = 0 \cdot 082$	$\log_e k_2 = 31 \cdot 55 - 21{,}700/RT$ $k_2^{50°} = 0 \cdot 101$
E2	$\log_e k_2 = 32 \cdot 13 - 22{,}100/RT$ $k_2^{50°} = 0 \cdot 097$	$\log_e k_2 = 33 \cdot 34 - 22{,}640/RT$ $k_2^{50°} = 0 \cdot 140$
S_N2 + E2	$\log_e k_2 = 31 \cdot 80 - 21{,}490/RT$ $k_2^{50°} = 0 \cdot 179$	$\log_e k_2 = 33 \cdot 28 - 22{,}250/RT$ $k_2^{50°} = 0 \cdot 241$

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51. *The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part VII. Attack at a Saturated Carbon Atom by a Charged Ion.*

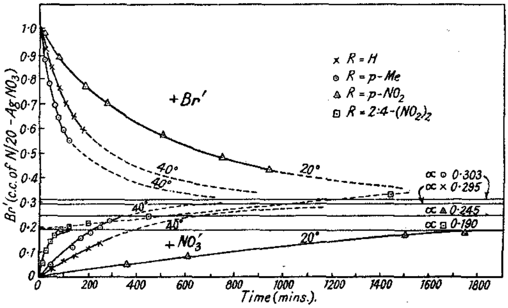
By JOHN W. BAKER and WILFRED S. NATHAN.

IN Part III (J., 1935, 519) it was suggested that a study of the equilibrium

$$C_6H_4R\cdot CH_2Br + CH_2Ph\cdot\overset{+}{N}C_5H_5\}\overset{-}{N}O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_4R\cdot CH_2\cdot O\cdot NO_2 + CH_2Ph\cdot\overset{+}{N}C_5H_5\}\overset{-}{B}r$$

should furnish information regarding reactions involving attack at a saturated carbon atom by a charged ion instead of by a neutral molecule. In $0 \cdot 025M$-solution in dry acetone, this equilibrium is established at a velocity convenient for kinetic study, and this paper records the data obtained in such an investigation, more especially with reference to the effect of the substituent R upon the values of k_1 and k_2.

FIG. 1.



It was first established, experimentally, that the same position of equilibrium was attained by starting from either pair of reactants (see Fig. 1, where typical results are plotted). Hence the kinetics of a reversible bimolecular reaction may be applied. If the initial concentrations (a) of the aryl bromide and of the arylpyridinium nitrate are equal, and x is the amount of aryl nitrate and arylpyridinium bromide formed at time t, we have

$dx/dt = k_1(a - x)^2 - k_2x^2$. If Δ is the value of x at equilibrium, integration of this equation in a manner similar to that employed by Bodenstein (*Z. physikal. Chem.*, 1894, **18**, 99) affords the relationship

$$k_1 = \frac{\Delta}{2at(a - \Delta)} \cdot \log_e \frac{\Delta a - x(2\Delta - a)}{a(\Delta - x)}$$

Use has been made of this expression to determine k_1 and k_2 independently from the experimental data, the procedure being to plot the values of the expression $f(x) = \log_{10}\{[\Delta a - x(2\Delta - a)]/a(\Delta - x)\}$ against time. The mean value of k_1 or k_2 was then derived from the slope of the best straight line drawn through the points so obtained. The results are summarised in Table I: concentration is expressed in g.-mols./l., time being in seconds. The experimental values of k_1 and k_2 are those obtained directly by using the appropriate pair of reactants. The calculated values are those derived from the relationship $K = k_1/k_2$ and the appropriate experimental value of k_2 or k_1, respectively.

TABLE I.

Data for the equilibrium

$$C_6H_4R{\cdot}CH_2Br + \bar{N}O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_4R{\cdot}CH_2{\cdot}O{\cdot}NO_2 + \bar{B}r$$

in 0·025*M*-solution in dry acetone.

			$k_1 \times 10^4$.		$k^2 \times 10^4$.		Arrhenius *E*, kg.-cals.			10^{-11} *PZ* (at 40°) for	
R.	Temp.	*K*.	Exp.	Calc.	Exp.	Calc.		k_1^R/k_1^H.	k_2^R/k_2^H.	k_1.	k_2.
H	20°	0·177	*0·60*	0·60	*3·33*	3·4	18·4	1	1	—	—
H	40	0·175	*4·33*	4·4	*25·0*	25·0		1	1	0·03	0·17
p-Me	20	0·189	*1·1*	1·4	7·3	*5·9*	18·9	1·8	1·75	—	—
p-Me	40	0·189	7·5	*8·8*	*46·3*	40		2·0	1·9	0·11	0·72
p-Et	40	0·170	*7·1*	—	—	*41·7*	—	$1·6_5$	1·7	—	—
p-Bu$^\gamma$	40	0·189	*6·8*	—	—	*36·6*	—	1·6	1·5	—	—
p-NO_2	20	0·105	*1·05*	1·04	*9·9*	9·9	18·9	$1·7_6$	3·0	—	—
p-NO_2	40	0·105	*8·2*	9·3	91	*78*		1·9	3·1	0·13	1·21
2 : 4-$(NO_2)_2$*	20	0·055	*4·0*	—	—	*76·7*	18·9	6·7	23	—	—
2 : 4-$(NO_2)_2$	40	0·055	*33·3*	—	—	*613*		7·7	24·5	0·52	9·5

The values printed in italics are those obtained from the more reliable experimental data and used in computing the other columns of the table.

* Although there is no doubt about the order of magnitude of the values for this compound, the actual figures are a little uncertain for the reason given on p. 241.

Confirmation that a true equilibrium is established is provided by some preliminary data, recorded in Table II, in which the initial concentrations of the aryl bromide (a) and the quaternary nitrate (b) were, respectively, 0·025 and 0·0125 g.-mols./l. Integration of the equation $dx/dt = k_1(a - x)(b - x) - k_2x^2$, giving the relationship when the initial concentrations of the two reactants are different, does not seem to be on record. We are greatly indebted to Dr. W. Wild, of this University, for the following integration. At equilibrium ($x = \Delta$), we have $k_2 = k_1(a - \Delta)(b - \Delta)/\Delta^2$; hence

$$dx/dt = k_1(a - x)(b - x) - k_1(a - \Delta)(b - \Delta)x^2/\Delta^2$$

and $$\int_0^t k_1 ab \,.\, dt = \int_0^x \left\{1 - \Delta\left(\frac{a+b}{ab}\right)\left(\frac{x}{\Delta}\right) - \left[1 - \Delta\left(\frac{a+b}{ab}\right)\right]\left(\frac{x}{\Delta}\right)^2\right\}^{-1} dx$$

giving $$k_1 = \frac{\Delta}{\{2ab - \Delta(a + b)\}t} \cdot \log_e \frac{ab\Delta - x\{\Delta(a + b) - ab\}}{ab(\Delta - x)}$$

From this expression the values of k_1, given in Table II, were determined. From the experimental value of K, k_2 was then calculated. It will be observed that the values obtained approximate closely to those observed when equimolecular concentrations were employed (Table I).

TABLE II.

$c_a = 0{\cdot}025$, $c_b = 0{\cdot}0125$ in dry acetone at 40°.

R.	K.	$k_1 \times 10^4$.	$k_2 \times 10^4$ (calc.).
H	0·18	4·5	25
p-Me	0·18	8·3	46
$p\text{-}NO_2$	0·10	9·2	92

The values of k_1 and k_2 should be affected by at least three main factors, *viz.*, (1) the ease of anionisation of the bromine atom (k_1) or the nitrate group (k_2); (2) the ease of co-ordination of the nitrate ion (k_1) or the bromide ion (k_2); (3) orientation effects in the approach of the nitrate ion (k_1) or the bromide ion (k_2) to the carbon atom of the methylene group in the compound $Ar{\cdot}CH_2{\cdot}X$. Data obtained in earlier parts of this series suggested that some information with regard to factor (1) should be obtained by a comparison of the velocities of interaction (k_p) of the aryl bromide and of the aryl nitrate, severally, with pyridine in dry acetone solution. In such quaternary-salt formation all the important factors involved may be assumed to be nearly identical, with the exception of the relative ease of anionisation of the bromide and the nitrate group from the aryl compound. Thus, *ceteris paribus*, the relative velocities should be very closely related to (I). At 40° the experimental value of k_p for benzyl nitrate is $0{\cdot}023 \times 10^{-4}$, *i.e.*, more than 200 times smaller than that ($4{\cdot}817 \times 10^{-4}$) for the corresponding reaction between pyridine and benzyl bromide under the same conditions.

Discussion.—Examination of the data summarised in Table I leads to the following conclusions.

1. Between 20° and 40° the position of equilibrium attained by any one pair of reactants is, within the experimental error, independent of temperature, *i.e.*, the activation energies of *the forward and reverse reactions are identical.*

2. This energy of activation (18·5—19 kg.-cals.) is approximately constant, *i.e.*, it is independent of the nature of the substituent group in the aryl bromide or nitrate. It is considerably higher than that observed (*ca.* 12·5 kg.-cals.; cf. Parts III and IV) for the attack on the aryl bromide by the neutral molecules pyridine and α-picoline in the same solvent. This is in agreement with our earlier suggestion (Part III, p. 523) that, when the attack at a saturated carbon atom is by a negatively charged ion instead of by a neutral molecule, penetration of the electronic field surrounding the saturated atom by the attacking ion might involve an increase in the critical energy increment of the reaction.

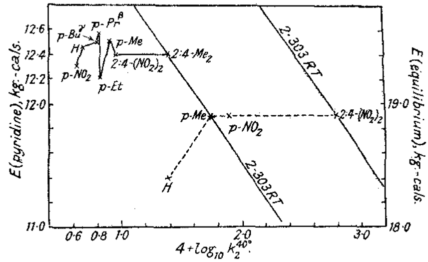
3. In all cases the position of equilibrium is displaced largely in favour of the aryl bromide–quaternary nitrate pair, the value of k_2 being from 5 (H) to 20 (2 : 4-dinitro) times as great as that of k_1. This larger value of k_2 might be due either (*a*) to the greater ease of ionisation of the $C{-}O{\cdot}NO_2$ than of the C–Br linking, or (*b*) to the greater efficiency of the attack by the bromide ion than by the nitrate ion. Since, with pyridine, the aryl nitrate reacts very much more slowly than the aryl bromide (above), the former explanation would seem to be extremely improbable. Hence, it must be concluded that the attack by the bromide ion at the saturated carbon atom is much the more effective, so much so, indeed, that this factor quite outweighs the less ready anionisation of the nitrate group.

4. As expected, since both the forward and reverse reactions involve interaction between a neutral molecule and a charged ion, the value of PZ in the equation $k = PZe^{-E/RT}$ approximates to the normal value $2{\cdot}8 \times 10^{11}$ (Moelwyn-Hughes, "Kinetics of Reactions in Solution," p. 82), *i.e.*, P is of the order of unity. The increase in velocity ($k_1 + k_2$) caused by introduction of substituents into the aryl bromide (or nitrate) (an increase amounting to over 20-fold in the case of the 2 : 4-dinitro-compound) is, however, again *found to be due, not to variation in E, but almost entirely to variation in the P factor.* In view of the recent findings of Winkler and Hinshelwood (J., **1935**, **1147**) that the most important factor determining variation in the velocity of interaction of various alkyl halides with tertiary bases is the energy of activation, it seems desirable to emphasise that *this does not appear to be so in the case of substituted benzyl halides.* Both in their reaction with tertiary bases (Parts III and IV) and in the equilibrium reaction discussed

above, variations in velocity (admittedly of a relatively small magnitude) seem to be accounted for almost entirely by corresponding variations in the *P* factor. This is shown clearly in Fig. 2, where the plot of log *k* against *E* (for both reactions) is oriented to a line of standard slope 2·303*RT* (Winkler and Hinshelwood, *loc. cit.*; compare, however, Hughes, Ingold, and Shapiro, preceding paper).

The effect of substituent groups upon velocity. The lack of variation in *E* and the bimolecular kinetics of the above equilibrium suggest that, as in the case of attack by a neutral pyridine molecule, the reaction involves essentially the electron cycle $\overset{\ominus}{A}\ CH_2Ar{-}X \longrightarrow A{-}CH_2Ar + \overset{\ominus}{X}$, in which the factors (*a*, anionisation) and (*b*, electrostriction of the attacking negative ion) cannot be differentiated. Since the velocity is increased by introduction either of electron-repelling alkyl groups, which will facilitate (*a*), or of electron-attracting nitro-groups, facilitating (*b*), the hypothesis of critical initiation of the electron cycle previously proposed (Part IV) may also be applied in this case. In the equilibrium studied, however, the minimum velocity is observed with the unsubstituted compound. Alkyl substituents appear to increase the values of k_1 and k_2 to approximately the same

FIG. 2.



——— $C_6H_4R{\cdot}CH_2Br + C_5H_5N$.
- - - - $C_6H_4R{\cdot}CH_2Br + NO_3'$ (*equilibrium*).

extent. This suggests that their polar influences are largely in the direction of increasing a pre-existing tendency to react by initiation of type (*a*) in both the aryl bromide and the aryl nitrate. Incidentally, it should be noted that their order of facilitation, Me>Et>Bu$^\gamma$, is again the reverse of that deduced from the operation of purely inductive (+ *I*) effects, and confirms our earlier views (Parts V and VI) regarding the electron-release capacity of the methyl group in such systems.

The introduction of electron-attracting nitro-groups, however, although also causing an increase in the value of k_1, effects a much greater increase in k_2, *i.e.*, it favours preferentially, attack by the bromide ion.

It would appear probable that in the *p*-nitro- and the 2 : 4-dinitro-derivative the critical point has been shifted in favour of (preferential) initiation of type (*b*), and the dominant factor has now become the electrostriction of the attacking anion at the α-carbon. It is therefore in this region that the importance of the orientation of the attacking ion becomes paramount. The size and structure of the two ions are pertinent factors relevant to this question. The radius of the bromide ion, determined by *X*-ray examination of the crystals of metallic bromides (Landolt–Börnstein, Erganzbd. II, p. 68), is 1·96 Å., and hence the most probable picture of the bromide ion in solution would represent it as a sphere of diameter approximately 3·92 Å. with one negative charge uniformly distributed on the surface. The nitrate ion has been shown (Goldschmidt, Freudenberg's "Stereochemie," 1933, p. 50) to possess a plane symmetrical structure, the distance between the nitrogen

and oxygen atoms being 1·23 Å. The ion is degenerate, two negative charges being distributed between the three oxygen atoms (located at the corners of an equilateral triangle) and one positive charge residing upon the nitrogen (situated at the centre of the triangle). Thus the bromide ion would seem to have a slightly larger collisional diameter. It is suggested that the difference in the effectiveness of attack by the two ions is mainly dependent upon their difference in structure. The spherical bromide ion, with its uniformly distributed negative charge, should be equally effective in promoting a critical collision no matter what is its orientation at the moment of approach to the saturated carbon atom. Orientation factors should, however, be much more important in relation to the similar attack by the nitrate ion. For any collision to be effective in promoting interaction, it seems probable that one of the oxygen atoms must be brought in close juxtaposition to the methylene carbon atom. Moreover a "flat-on" approach of the plane nitrate ion would present the central, positively charged nitrogen atom to the positive methylene carbon atom, thus bringing into play repulsive forces very unfavourable for the interpenetration of the electronic fields surrounding the reacting entities. Such orientation phenomena are at least in qualitative agreement with our results. The strong electron attraction of nitro-groups in the *o*- and *p*-positions to the side chain will greatly increase the positivity of the methylene carbon, thus facilitating the close approach of the symmetrically charged bromide ion, and so, greatly increasing the value of k_2. This induced field at the methylene carbon atom should also favour the approach of the attacking nitrate ion, but, because of the rather special orientation necessary in this case, the increase produced in k_1 is of a much smaller magnitude.

EXPERIMENTAL.

Preparation of Materials.—Benzyl nitrate was prepared by Nef's method (*Annalen*, 1899, **309**, 171). It was not readily purified, for it retained a small amount of an impurity (probably nitrogen-free), difficult to remove by distillation. Purification was controlled by heating the sample with an excess of pyridine at 100° for several hours, and determination of the nitrate ion so produced gravimetrically as nitron nitrate. Repeated distillation over silver nitrate gave the ester as a colourless liquid, b. p. 43°/0·5 mm. (Found : C, 55·5; H, 4·65; N, 9·5; NO_3', 39·9, 40·6. Calc. for $C_7H_7O_3N$: C, 54·9; H, 4·6; N, 9·2; NO_3', 40·5%).

p-*Methylbenzyl nitrate* was similarly prepared from *p*-methylbenzyl bromide and pure silver nitrate. A similar purification gave the nitrate as a colourless liquid, b. p. 60°/0·2 mm. (Found : NO_3', 36·6. $C_8H_9O_3N$ requires NO_3', 37·1%). A sample, b. p. 73·0°/0·6 mm., from which the final sample was obtained by two further distillations, was analysed completely (Found : C, 58·0; H, 5·7; N, 7·7; NO_3', 34·6. $C_8H_9O_3N$ requires C, 57·5; H, 5·4; N, 8·4; NO_3', 37·1%). The agreement between the values for N and NO_3' indicates that the impurity is probably nitrogen-free.

p-Nitrobenzyl nitrate (Staedel, *Annalen*, 1883, **217**, 214) had m. p. 69°.

The substituted benzyl bromides were the specimens used for velocity determinations in earlier parts of this series. From them, the benzylpyridinium bromides were obtained by direct interaction with pyridine. Benzylpyridinium bromide is very hygroscopic and was dried over phosphoric oxide for several months before analysis (Found : Br, 31·86. Calc. for $C_{12}H_{12}NBr$: Br, 31·96%). *p*-Nitrobenzylpyridinium bromide has m. p. 218—220° (decomp.) (Found : Br, 27·08. Calc. for $C_{12}H_{11}O_2N_2Br$: Br, 27·09%). By interaction of the quaternary bromides with exactly the theoretical amount of aqueous silver nitrate were obtained *benzylpyridinium nitrate*, extremely hygroscopic (Found : NO_3', 26·1. $C_{12}H_{12}O_3N_2$ requires NO_3', 26·7%) and p-*nitrobenzylpyridinium nitrate*, m. p. 186° (decomp.) after crystallisation from 90% alcohol (Found : C, 52·2; H, 4·2. $C_{12}H_{11}O_5N_3$ requires C, 52·0; H, 4·0%).

The acetone was the unreactive sample used in Part IV.

Velocity Determinations.—The velocity measurements were effected by determination of the bromide ion by means of the micro-technique previously described (Part IV). Owing to their hygroscopic character, the solutions of the quaternary salts were made by tipping approximately the required amount of the dry salt from a small dried weighing tube directly into a known volume of dry acetone and determination of the weight used by difference. The solution was then diluted (in the thermostat) with the necessary volume of dry acetone to reduce the concentration to 0·05*M*. The aryl bromide or nitrate solutions (0·05*M*) were made up by direct weighing. 10 C.c. of each solution were then mixed at the temperature of the thermostat.

The position of equilibrium, in each case, was separately determined on solutions kept in sealed tubes in the thermostat for the necessary period.

In all cases, except that of the 2 : 4-dinitro-derivative, the plot of $f(x)$ (p. 237) against time gave, within experimental error, a straight time, from the slope of which the mean value of the velocity coefficient was determined. In the case of the 2 : 4-dinitrobenzyl bromide, the plot of the actual titrations against time showed the usual curve approaching an equilibrium value, followed by a slow further increase in titre directly proportional to time (see Fig. 1). The cause of this secondary reaction is unknown, but the equilibrium position was determined approximately by extrapolation of the straight line portion of the curve back to the titre-axis. For this reason the actual values of k_1 and k_2 are a little uncertain in this case, but their relative magnitude is beyond doubt. The possibility of reaction with the cation

$$C_6H_4R{\cdot}CH_2Br + CH_2Ph{\cdot}\overset{+}{N}{\cdot}C_5H_5 \rightleftharpoons CH_2Ph{\cdot}Br + C_6H_4R{\cdot}\overset{+}{N}C_5H_5$$

has been considered, but owing to the small solubility of the nitrobenzylpyridinium bromide in dry acetone direct experimental investigation of this possibility was not possible.

Interaction of Benzyl Nitrate with Pyridine in Dry Acetone.—The velocity of quaternary salt formation was determined exactly as previously described in the case of the quaternary bromide, except that the reaction was followed by gravimetric determination of the nitrate ion produced. For this purpose the following micro-technique was evolved. A 2-c.c. sample of the reaction solution (originally 0·025*M* with respect to both reactants) was run into a specially constructed 15—20 c.c. separating funnel containing 2 c.c. of water and 10 c.c. of ether. After shaking, the aqueous layer was separated, and extraction of the ethereal layer repeated twice with 1 c.c. portions of water. The aqueous solution remaining in the short, drawn-out stem of the funnel was washed out with 0·5 c.c. of water. The combined aqueous extracts were evaporated on the steam-bath until their volume was reduced to 3—4 c.c. To the hot solution 3 drops of acetic acid and 25 drops of a standard nitron solution (Treadwell and Hall, " Analytical Chemistry," Vol. 2, p. 451) were added. The solution was allowed to cool to room temperature, and was then kept in ice for 30 minutes, access of air and light being minimised to prevent oxidation of the nitron. The precipitated nitron nitrate was collected in a weighed micro-crucible fitted with a fused-in porous bottom, washed with 2 c.c. of water saturated with nitron in small portions, and dried at 110° for 30 minutes before weighing. Under these conditions the factor NO_3'/nitron nitrate = 16·79%. The accuracy of the method was tested first on pure sodium nitrate in 0·025*N*-solution (Found : NO_3', 71·3, 71·5. Calc. for $NaNO_3$: NO_3', 72·9%), and then with 2 c.c. of a 0·025*M*-solution of benzylpyridinium nitrate in dry acetone, treated as above (Found : NO_3', 26·57, 26·42. Calc. for $C_{12}H_{12}O_3N_2$: NO_3', 26·1%). A control experiment, in which a solution of benzyl nitrate in acetone was similarly treated, gave no precipitate of nitron nitrate.

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THE UNIVERSITY, LEEDS. [*Received, December 23rd*, 1935.]

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52. *The Photochemical Union of Hydrogen and Chlorine. Part IV. The Reaction at Low Hydrogen Pressures. Effects of Wave-length, of Temperature and of Traces of Oxygen.*

By H. C. CRAGGS and A. J. ALLMAND.

THE work now described forms part of a more comprehensive study of the union of hydrogen and chlorine at low hydrogen pressures undertaken during the period 1930—1933. The experimental method will be described in detail later. It was similar to that devised by Rollefson (*J. Amer. Chem. Soc.*, **1929**, **51**, 770) and used by Bateman and Craggs (*Trans. Faraday Soc.*, **1931**, **27**, 445), the pressure of chlorine being kept constant throughout an experiment by the immersion of a side-tube of the apparatus, containing liquid or solid chlorine, in a bath of refrigerant, and the pressure of hydrogen being measured by means of a mercury-in-glass Pirani gauge, after chlorine and hydrogen chloride had been frozen

out by means of liquid air. Reaction vessels both of quartz and of glass were used. Chlorine was taken from a cylinder and distilled in a vacuum before being condensed in the reaction system. Its pressure was varied between 0·012 and 166 mm. Hydrogen was admitted by means of a palladium tube; its pressure was usually of the order of 0·1 mm.

The rate was found to be essentially proportional to the hydrogen pressure, and the effect of varying any particular condition was expressed in terms of its effect on the *slope*, this being defined as $-100\,(\Delta \log p_{H_2}/\Delta t)$, where p and t are in mm. and minutes respectively. The only other result which need be quoted at this stage is the effect of light intensity. Briefly, we found n, in the expression Rate $\propto I_0^n$, to be practically unity at the lowest chlorine pressures used, and to fall continually as p_{Cl_2} increased, the lowest value observed by us being 0·6—0·7 at 166 mm. of chlorine.

Experimental.

Reaction at 546 μμ.—Previous work with moist electrolytic gas at 1 atm. pressure containing traces of oxygen (Parts II and III, J., 1930, 2709; 1934, 157) had shown light at 546 μμ to be active in causing the combination of hydrogen and chlorine, in agreement with less specific conclusions of earlier workers. The mechanism of reaction in this region is not immediately obvious, and on that account it seemed desirable to test the point again under our modified experimental conditions, *i.e.*, working at low pressures of hydrogen and in absence of oxygen. The preliminary experiments were done by using a similar compound filter to that employed in Part II (*loc. cit.*, p. 2711). The light source was a 100-volt quartz-mercury lamp, used without any diaphragm in order to get the maximum available intensity. The results were inconclusive, in that, whilst a definite reaction was obtained, the use of an additional filter showed that traces of light of shorter wave-length than 546 μμ were also present. It was therefore decided to work with the large monochromator used in Part III. A series of careful preliminary measurements was first carried out, in which the prism drum of the monochromator was set at various readings adjacent to those corresponding to the different mercury lines, and the values plotted against the deflexions given by a combination of a linear thermopile, placed in an air-tight case behind the telescope slit, and a Zernicke moving-coil galvanometer. The light source was a 200-volt vertical atmospheric mercury arc, the radiation being concentrated on the collimator slit by means of a quartz lens. The relative intensities of the mercury lines were estimated in this way, and an idea obtained of the magnitude of the stray light energy which might be expected to be present when using the instrument. This proved to be small, as the following typical examples show:

313 μμ.		546 μμ.	
Drum reading.	Deflexion, mm.	Drum reading.	Deflexion, mm.
672	5	846	10
678	575 (maximum)	851	1120 (maximum)
685	5	855·5	15

Similar results were obtained in all other cases, and indicate that the proportion of stray light to be expected when working with one of the mercury lines is about 1%, distributed over the whole of the spectrum. This proportion is insufficient to affect the measurements recorded later of relative quantum yield except (see remarks on Expts. 84—88 below) when the extinction coefficient of the gas for the wave-length under investigation is particularly low.

In the experiments which follow, the usual quartz apparatus was employed, completely sealed off from pump and palladium tube after introduction of the gases. The prism drum was set to 546 μμ. The linear thermopile was removed from the telescope slit, and the emergent light converted by a cylindrical quartz lens into a beam which passed through the reaction vessel. The small percentage of stray light in the beam was still further reduced by the use of two filters, chosen to cut out all light below 546 μμ. Of these, I transmitted 59·4% at 546 μμ, and II, which also cut out yellow and red light, 11%. Neither passed detectable amounts at 436 μμ. The results are summarised in Table I. The figures in parentheses in the last column denote slopes which are zero within the experimental error.

Expts. 81—83*a*, in which the slope decreased as the monochromator setting moved towards the blue, show very clearly that the action at 546 μμ is not due to stray light of short wave-length, but to the mercury-green line itself, a conclusion confirmed by Expts. 90—93. In the

TABLE I. (Series 16.)

Expt.	Filter.	Monochromator setting, $\mu\mu$.	Cl_2, mm.	HCl, mm.	Initial H_2, mm.	Final H_2, mm.	Total time, mins.	Mean slope.
81	I	546	45·7	0·00	0·605	0·545	784	0·0058
82	I	520	,,	0·12	0·545	0·540	438	0·0009
83	I	492	,,	0·12	0·540	0·538	266	(0·0006)
83*a*	I	436	,,	0·12	0·538	0·538	257	zero
84	None	546	,,	0·12	0·538	0·4345	291	0·0319
85	None	520	,,	0·34	0·4345	0·404	117	0·0270
86	None	534	,,	0·40	0·404	0·379	113	0·0246
87	None	492	,,	0·44	0·379	0·340	104	0·0467
88	None	436	,,	0·52	0·340	0·2145	4	5·0
89	I	546	166	0·86	0·1726	0·1668	321	0·0046
90	II	436	45·7	0·90	0·1480	0·1479	150	(0·0002)
91	II	546	,,	0·90	0·1479	0·1457	416	0·0016
92	I	546	,,	0·90	0·1457	0·1425	185	0·0052
93	I	492	,,	0·90	0·1425	0·1424	195	(0·0002)

absence of a filter, Expts. 84 and 86 show the same tendency; but the slopes then begin to rise as the monochromator is set at shorter wave-lengths. This in undoubtedly due to the stray light which, although present in small quantity, will be relatively very strongly absorbed in this region (absorption at 366 $\mu\mu$, 405 $\mu\mu$, 436 $\mu\mu$, and 546 $\mu\mu$ respectively about 98, 42, 20, and 0·03%). Most of the reaction in Expt. 84 must be attributed to this 1% of stray light. This is confirmed by the fact that, whilst the transmissions of Filters I and II at 546 $\mu\mu$ are 59·4 and 11%, the corresponding slopes in Expts. 81, 92, and 91 are respectively only about 18, 17 and 5% of that in Expt. 84. In the relative measurements of γ, described later, this stray light effect will play quite a minor part (except when working with 546 $\mu\mu$); the difference between its average extinction coefficient and that of the light rays actually under study is far smaller than, indeed of quite a different order from, that in the present case. The ratio of the slopes in Expts. 81 and 91 corresponds to an n value of 0·76, and that of Expts. 91—92 to $n = 0{\cdot}70$. The value deduced earlier for white light at this pressure was 0·76. Taking this figure as a basis, we can calculate that about three-quarters of the observed reaction in Expt. 84 was due to stray light.

Reaction at 579 $\mu\mu$.—Between Expts. 88 and 89, two experiments were carried out in the same way as above, using the monochromator in conjunction with a yellow Corning filter G.34R, which transmits only 1% of the 546 $\mu\mu$ line. At 45·7 mm. of chlorine, the slope over a 2-hour period was zero within the experimental error. At 166 mm. there was a very doubtful reaction in 11 hours (no pressure change during two out of the four time intervals into which the experiment was divided). Any reaction at 579 $\mu\mu$ would be expected to have a very high temperature coefficient. Consequently, an experiment lasting 22 hours was done with 45·7 mm. of chlorine at 57° by the methods described below. Again, the slope was practically zero, and *less* than in the experiment at room temperature. We conclude therefore that, although all three experiments gave very slight pressure decreases (severally 0·0005, 0·0052, and 0·0013 mm.), these are due to erroneous pressure readings, and that light of this wave-length is inactive.

Effect of Temperature at 436 $\mu\mu$ *and* 546 $\mu\mu$.—Earlier work, both experimental and theoretical, had indicated that the temperature coefficient in green light, reaction being assumed to take place, would be considerably higher than that in the continuous spectrum region. The experiments just described show conclusively that the reaction can proceed in monochromatic light of λ 546 $\mu\mu$, and we consequently undertook measurements of the temperature coefficient at this wave-length and at 436 $\mu\mu$, which lies well within the continuum. For this purpose, the reaction vessel was jacketted by a thin copper sheet projecting about 4 cm. beyond the ends of the cell, then wound with a uniformly spaced coil of resistance wire and covered with a thick layer of asbestos string. A thermometer inserted in a socket in the copper jacket indicated the temperature of the cell, which was heated electrically to about 57°, at which temperature it could readily be kept constant by slight adjustments of an external resistance. Three experiments were done with 546 $\mu\mu$ light, alternating with two at room temperature. These were followed by similar experiments with the 436 $\mu\mu$ line. When working at 57°, the cell, subsequently to Expt. 97, was kept at this temperature for at least 12 hours prior to illumination, as in this case the slope rose considerably during the first few insolations and was still rising at the end, suggesting that temperature equilibrium had not been reached. This was not observed at room temperature. All experiments were carried out at $p_{Cl_2} = 45{\cdot}7$ mm., and Filter I was used when working with 546 $\mu\mu$. In Expts. 97—101 (duration of insolation, 5—20

hours) the slopes given are the final ones observed. In Expts. 102—104, lasting a few minutes only, the slopes are the average figures. The results are given in Table II.

TABLE II. (Series 18.)

Expt.	λ, μμ.	Initial H_2, mm.	Final H_2, mm.	Slope.	Cell temp.	Expt.	λ, μμ.	Initial H_2, mm.	Final H_2, mm.	Slope.	Cell temp.
97	546	0·1533	0·1270	0·0173	57·0°	101	546	0·0983	0·0815	0·0215	57·3°
98	546	0·1183	0·1127	0·0033	18·3	102	436	0·0821	0·0365	8·80	57·4
99	546	0·1214	0·1072	0·0211	57·0	103	436	0·0340	0·01718	2·97	16·9
100	546	0·0998	0·0916	0·0031	18·0	104	436	0·01760	0·00527	7·48	57·7

Before comparing the slopes at the two room temperatures, it is necessary to correct for the fact that the chlorine concentration at the higher temperature will be less than at the lower temperature, the pressure in both cases being controlled at 45·7 mm., and that therefore the amount of light absorbed will be correspondingly less. On the assumption that the extinction coefficients are independent of temperature, the corresponding factors are 0·89 at 436 μμ and 0·88 at 546 μμ. Taking the intensity exponent *n* as 0·76, the slopes at 57° in absence of any specific temperature effect become respectively $2{\cdot}97 \times (0{\cdot}89)^{0{\cdot}76}$ and $0{\cdot}0032 \times (0{\cdot}88)^{0{\cdot}76}$. We thus obtain the results in Table III for the higher temperatures. (Expt. 97 is omitted for the reason given above.)

TABLE III.

Expt.	λ, μμ.	Slope. Calc. in absence of temperature effect.	Slope. Found.	Temp. coeff. for 10° rise. Average.	Temp. coeff. for 10° rise. 17—27°.	*E*, kg.-cals.
99, 101	546	0·00290	0·0213	1·667	1·760	9·78
102	436	2·72	8·80	1·335	1·374	5·50
104	,,	,,	7·48	1·282	1·315	4·74

The increased activation required for the reaction at 5461 Å. as compared with that in the continuum is therefore given by Expt. 102 as 4·3 kg.-cals., and by Expt. 104 as 5·0 kg.-cals.

Effect of Wave-length on Quantum Efficiency.—Previous workers in this laboratory investigating this subject had used a form of Bunsen actinometer and electrolytic gas containing traces of oxygen. It was considered advisable to see whether their most striking result, *viz.*, the fall in γ when passing from the visible to the ultra-violet spectrum, could be reproduced when working at low hydrogen pressures, and in absence of both water vapour and oxygen. The technique of following the reaction was as before, inlet tnbes for both hydrogen and chlorine being sealed off after the gases had been introduced. The light source was a 200-volt mercury arc, used in conjunction with the large monochromator, the beam from the telescope slit being concentrated on the cell by means of a cylindrical quartz lens. The energy distribution in the radiation was determined by a calibrated thermopile as already described, and the results applied directly when working with all-quartz apparatus. In one series (20), a glass plate was present on the back of the thermopile chamber. In this case, the emergent light was brought to a focus on a calibrated 2-cm. Moll surface thermopile, and the relative intensities of the lines thus compared. In order to concentrate all the issuing light on the thermopile for this purpose, the height of the telescope slit had to be cut down by means of a diaphragm. The relative rates of quantum absorption at any given wave-length and pressure were calculated by combining the above data with the extinction coefficients determined by von Halban and Siedentopf (*Z. physikal. Chem.*, 1922, **103**, 71).

The measurements on which we place most reliance were carried out with 1·7 mm. of chlorine. Under these conditions, the intensity exponent *n* is 0·97—0·98, and hence the quantum efficiency is almost independent of moderate variations of intensity. We also did measurements with 313 μμ and 436 μμ at 0·11 mm. of chlorine. But in order to obtain comparative results with the weakly absorbed lines at 254 μμ and 546 μμ, it became necessary to work with higher chlorine pressures. Measurements at 45·7 mm. were therefore undertaken. Their interpretation introduced a difficulty, for at such pressures, *n* is far removed from unity, and consequently, using light beams of widely differing intensity and extinction coefficient, any specific effect on γ of change in λ tends seriously to be masked by the effect due to the changes in rate of quantum absorption. There is really no satisfactory way of overcoming this difficulty. In practice, we determined the slope at 436 μμ by two experiments in which the intensities varied in the ratio of 1 : 1·93. The resulting intensity exponent was found to be 0·69, and this figure,

and also the considerably higher one (0·76) regarded by us, from the general nature of our unpublished data, as normal for these pressures, were both used to correlate the data at different wave-lengths. The results of our three series of experiments are contained in Tables IV—VI, in which *r* denotes the relative absorbed quanta.

TABLE IV. (Series 20.)

p_{HCl} = 0·5 mm. initially, 1·58 mm. at end; p_{H_2} = 0·62 mm. initially, 0·08 mm. at end; p_{Cl_2} = 1·7 mm. in Expts. 108—117, 0·11 mm. in Expts. 118 and 119.

Expt.	λ, μμ.	Mean slope.	*r*.	Relative γ.	Expt.	λ, μμ.	Mean slope.	*r*.	Relative γ.
108	436	0·086	1·00	0·96	114	303	0·064	1·06	0·67
109	405	0·124	1·44	0·96	115	365	1·345	21·0	0·71
110	365	1·12	21·0	0·59	116	436	0·093	1·00	1·03
111	436	0·090	1·00	1·00	117	405	0·115	1·44	0·89
112	313	0·563	9·13	0·69					
113	436	0·095	1·00	1·06	118	313	0·0394	9·71	0·86
					119	436	0·0047	1·00	1·00

Mean relative γ values for Expts. 108—117: 436 μμ, 1·00; 405 μμ, 0·92; 365 μμ, 0·65; 313 μμ, 0·69; 303 μμ 0·67; for Expts. 118 and 119: 436 μμ, 1·00; 313 μμ, 0·86.

TABLE V. (Series 21.)

p_{HCl} = 0·0 mm. initially, 0·6 mm. at end; p_{H_2} = 0·538 mm. initially, 0·238 mm. at end; p_{Cl_2} = 1·7 mm. throughout.

120	436	0·0413	1·00	(0·61)	125	436	0·072	1·00	1·06
121	303	0·203	4·27	0·70	126	405	0·101	1·35	1·10
122	436	0·068	1·00	1·00	127	303	0·218	4·27	0·75
123	365	0·870	19·8	0·65	128	265	0·00369	0·0674	0·81
124	313	0·70	15·6	0·66					

Mean relative γ values: 436 μμ, 1·00; 405 μμ 1·07; 365 μμ, 0·63; 313 μμ, 0·64; 303 μμ 0·70; 265 μμ, 0·79.

TABLE VI. (Series 22.)

p_{HCl} = 0·76 mm. initially, 0·95 mm. at end; p_{H_2} = 0·164 mm. initially, 0·067 mm. at end; p_{Cl_2} = 45·7 mm. throughout.

Expt.	γ, μμ.	Mean slope.	*r*.	$r^{0.69}$.	Relative γ.	$r^{0.76}$.	Relative γ.
129 and 131	436	0·886	1·00	1·00	1·00	1·00	1·00
132	405	1·023	1·14	1·094	1·05	1·105	1·04
133	365	4·58	6·15	3·50	1·48	3·98	1·30
134	313	1·96	2·70	1·985	1·12	2·13	1·04
135	303	0·910	1·05	1·034	0·99	1·038	0·99
136	254	0·0218	0·0121	0·04764	0·52	0·0350	0·70
137	265	0·117	0·0693	0·1586	0·83	0·1315	1·00
139	546	0·0161	0·00268	0·01683	(1·08)	0·01112	(1·63)
140	436	0·810	1·00	1·00	0·91	1·00	0·91

Omitting Expt. 120, for the abnormal result of which we cannot account, and making due allowance for irregularities due to the fact that the 200-volt mercury arc used had to be run off the main supply and not off the Tirrill regulator, there can be little doubt that the figures in Tables IV and V confirm the results obtained in Parts II and III, in that γ falls off very definitely when passing from the visible to the ultra-violet spectrum. Table VI, however, appears to reveal a different state of affairs. In any case, the high values of γ indicated by Expt. 139 for green light are illusory. The conditions of insolation were the same as in Expt. 84 (Table I), and the observed values should be multiplied by about 0·25, which gives 0·3—0·4 as the true relative quantum efficiency. The figures in Expts. 133 and 134 depend on insolation times of 30 and 45 seconds respectively, and for that reason are perhaps not to be regarded as very reliable. These wave-lengths being omitted, it would appear that, if *n* is taken as 0·69, only the λλ 265 and 254 μμ give the anticipated low values of γ, whilst if 0·76, the "normal" value of *n*, be taken, then γ seems to be independent of wave-length (omitting the figure for 365 μμ, still abnormally high) from 436 μμ to 265 μμ. The figure for 254 μμ remains low, and the corresponding slope is probably quite sound experimentally; but the relative intensity of this line is particularly subject to fluctuations with changes in the energy input into the lamp. If, on the other hand, apart from Expt. 139, reliance is placed on the relative γ values in col. 6, it may be noted that, qualitatively, they fall in the same order as both the observed

slopes and the relative rates of quantum absorption, increasing from 254 $\mu\mu$, as wave-length increases, up to a maximum at 356 $\mu\mu$ and then falling off to 436 $\mu\mu$. This three-fold parallelism is not observed at 1·7 mm. of chlorine.

Our conclusion is that, at low pressures of hydrogen and of chlorine, γ falls off in the ultra-violet region just as was previously found for electrolytic gas containing traces of oxygen, but that, when the chlorine/hydrogen ratio is high, γ is constant down to, at all events, the neighbourhood of 260 $\mu\mu$. Figs. 1 and 2 summarise graphically the results obtained both in this paper and also in Parts II and III, with the exceptions of our Expts. 118 (discussed later), 120, and 133, as also the value for 405 $\mu\mu$ found in Part II, and attributed (see Part III) to a faulty light filter. In Fig. 1 are collected the results of all measurements with wave-lengths not $<$ 400 $\mu\mu$, together with the data for higher frequencies contained in Table VI, assuming $n = 0·76$; Fig. 2 includes all the data obtained with ultra-violet light which are recorded in Parts II and III and in Tables IV and V. The relative value of γ_{546} given in Part III has been

FIG. 1.

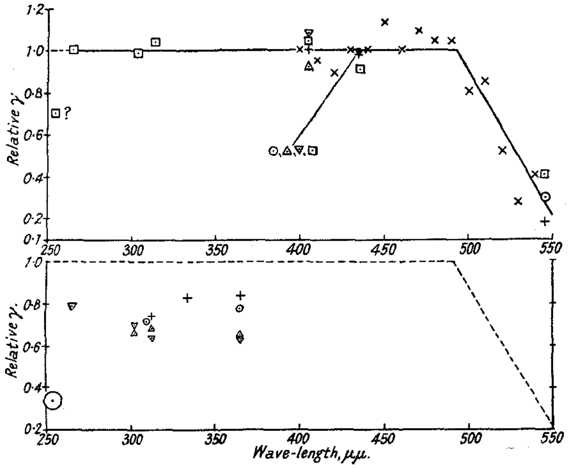

FIG. 2.

multiplied by 0·25, as was done in the case of Expt. 139, and for the same reason. The following notation is employed: Part II, ⊙; Part III, + and ×, for data from mercury-vapour and metal-filament lamp respectively; Table IV, △; Table V, ▽; Table VI, ⊡.

Experiments in Presence of Oxygen.—A few measurements were carried out with about 0·1 mm. oxygen present in the gas, their purpose being to verify the statement of Mrs. Chapman (J., 1923, **123**, 3062) that, at sufficiently low concentrations of hydrogen, oxygen does not act as an inhibitor.

The oxygen was introduced in known amount into the apparatus by heating to dull redness weighed quantities of silver oxide contained in a small side-tube, sealed on to the main apparatus, and separated from it by a tap lubricated with metaphosphoric acid. The whole was thoroughly evacuated, the tap closed, the oxygen liberated in the side-tube, and admitted into the main apparatus, with the chlorine frozen out, after the hydrogen had been added. The volume of the side-tube was negligibly small. The Pirani gauge was first calibrated for oxygen against a McLeod gauge. As $f(v)$ for a gaseous mixture is not the sum of the $f(v)$ values for its constituents (see, *e.g.*, *Proc. Roy. Soc.*, 1928, *A*, **121**, 344; 1932, **134**, 654), a second calibration

was then done, in which the voltage function was determined for various known hydrogen pressures to which 0·1 mm. of oxygen had been added, thus enabling p_{H_2} at any stage of the reaction to be deduced from the $f(v)$ for the hydrogen–oxygen mixture on the assumption that the oxygen pressure remained unaltered. This approximate method, with the necessary corrections for deviations in actual oxygen pressure from 0·1 mm., was considered sufficiently accurate for these experiments. The results are contained in Table VII. The oxygen pressures in the last column were direct measurements after all the hydrogen had been insolated away at the close of the experiment.

TABLE VII. (Series 12 and 13.)

Expt.	p_{Cl_2}, mm.	Initial p_{HCl}, mm.	Initial p_{H_2}, mm.	Final p_{H_2}, mm.	Slope.	*r*.	Relative γ.	Remarks.
63	1·7	0·72	0·280	0·0619	4·4	0·44	10	Rising slope.
64	13	1·14	0·0619	0·0132	6·7	2·0	3·4	
			0·0132	*0·0109*	0·24			
65	1·7	3·3	0·133	0·0185	3·4	0·44	7·7	
66	13	3·5	0·393	0·0356	26	8·74	3·0	p_{O_2}, 0·116 mm.
			0·0356	*0·0089*	2·0			
67	45·7	5·5	0·425	0·0259	13	3	4·3	
68	13·0	0·80	0·452	0·0101	4·6	2·0	2·3	Rising slope.
			0·0101	0·0052	0·56			p_{O_2}, 0·100 mm.
69	13·0	1·7	*ca.* 2	zero				p_{O_2}, 0·099 mm.
70	45·7	5·6	1·2	0·0352	7·7	3	2·6	p_{O_2}, 0·097 mm.
71	166	9·0	0·76	0·101	0·9	3·9	0·24	p_{O_2}, 0·094 mm.
72	166	11·0	154	zero				H_2 added by side-tube; p_{O_2}, 0·076 mm.
73	13	318	0·730	0·0118	1·09	8·7	0·12	p_{O_2}, 0·074 mm.
					0·38	2·0	0·19	HCl determined at end volumetrically after absorption in water.

A comparison between the slopes in Expts. 63 and 65 and those obtained in unpublished work shows 0·1 mm. of oxygen to have no appreciable retarding effect at 1·7 mm. pressure of chlorine. The same holds at 13 mm. of chlorine. Taking n as 0·89 in Expt. 64, the observed slope of 6·7 would become 25 at 8·7 units of absorbed intensity, and this figure and that in Expt. 66 compare well with the average slope of 27 found in absence of oxygen (unpublished). Similarly, the slope found in Expt. 68 (a somewhat uncertain result) agrees reasonably well with that obtained under similar conditions with oxygen-free gas. The results at 45·7 mm. of chlorine, on the other hand, are remarkable. Comparison between Expt. 70 and the corresponding one done in absence of oxygen leads to the conclusion, if both are reliable, that oxygen has markedly accelerated the reaction. Expt. 67 cannot be directly compared with any one done in the absence of oxygen, but its relative γ value is considerably higher than any other observed in our work at this chlorine pressure. Moreover, the results in Series 12, taken as a whole, indicate that, at the same incident intensity, $\gamma_{1\cdot7} > \gamma_{13} < \gamma_{45\cdot7}$, a type of relation not observed in any other of our experiments, although in unpublished work with oxygen-free mixtures we have found instances of $\gamma_{13} < \gamma_{45\cdot7}$. It is very difficult to imagine how oxygen could accelerate the reaction or why it should do so at one particular chlorine pressure. We can therefore offer no explanation for these results, and indeed only quote them because they appear to confirm one another. Expt. 71, at 166 mm. of chlorine, cannot be compared directly with any other done in the absence of oxygen, but there are certain indications, which we need not specify, that the oxygen has had little or no effect. We can therefore conclude from our experiments that, at hydrogen pressures above the order of 0·01 mm., an oxygen pressure of 0·1 mm. exerts no retarding influence.

Two further points remain for consideration. There is some evidence in Expts. 64, 66, and 68 that, at still lower pressures of hydrogen, a marked retarding effect of oxygen enters, the slope falling off to a far greater extent than was found in certain unpublished experiments in absence of oxygen. Moreover, although no retardation at the higher hydrogen pressures was observed, oxygen was consumed in the reaction. These two facts may possibly be connected, for, in order to substantiate the fact that oxygen was used up in an experiment, it was necessary at the end to continue the insolation until all the hydrogen had disappeared. They will be discussed later.

DISCUSSION.

The Reaction at 546·1 $\mu\mu$.—The experiments in Table I show conclusively that the light of the mercury-green line (546·1 $\mu\mu$; 18,300 cm.$^{-1}$; 52·0 kg.-cals.) brings about the reaction, a fact which raises points of interest. This line lies in the spectrum region of chlorine absorption characterised by bands which converge at about 478·5 $\mu\mu$ (20,900 cm.$^{-1}$; 59·4 kg.-cals.), a limit marking the threshold of the optical dissociation process $Cl_2(^1\Sigma_g) \longrightarrow Cl\ (^2P_{3/2}) + Cl\ (^2P_{1/2})$, the absorbing chlorine molecule being in its zero vibrational quantum state. The dissociation of the same molecule to two normal ($^2P_{3/2}$) atoms requires 56·8 kg.-cals. (500·0 $\mu\mu$; 20,000 cm.$^{-1}$). The absorption of a light quantum at 546·1 $\mu\mu$ is therefore, neither directly nor as the result of a subsequent collision, capable of dissociating such a chlorine molecule into its constituent atoms. On the other hand, we have seen that the reaction has a quantum efficiency of about 0·3 of the value in the neighbouring continuum; it therefore involves chains which, in all probability, are of the same atomic mechanism as when initiated by light of shorter wave-length.

A scheme of the type

$$\text{(i)}\ Cl_2 + 52\ \text{kg.-cals.} \longrightarrow Cl_2'$$
$$\text{(ii)}\ Cl_2' + H_2 \longrightarrow 2\ HCl^* + 96\ \text{kg.-cals.}$$
$$\text{(iii)}\ HCl^* + Cl_2 \longrightarrow HCl + Cl + Cl - 56{\cdot}8\ \text{kg.-cals.}$$

is thermochemically possible. But even if the relatively high temperature coefficient of the reaction in this region were to correspond to an extra activation heat of 4—5 kg.-cals. (Table III), making a total energy of 100—101 kg.-cals. available as the result of (ii), it would be necessary to assume that this energy has a high probability of unsymmetrical distribution between the two molecules of hydrogen chloride. More probable might be (i), followed by

$$\text{(iv)}\ Cl_2' + H_2 \longrightarrow HCl + H + Cl.$$

On the assumption just made, this step would be a thermoneutral one, and, for that reason, perhaps plausible. There are, however, at least two objections to such schemes. The relative γ value of about 0·3 at room temperature has been found, not only with gas mixtures containing 0·5 atm. each of hydrogen and of chlorine, but also with a mixture *of composition* Cl_2 *45·7 mm.;* H_2 *0·1 mm. To bring these results into line with the* above suggestion, it would be necessary to assume a very low deactivating efficiency for Cl_2'–Cl_2 collisions, which is unlikely. Further, and applying particularly to the second mechanism, if the high temperature coefficient at 546·1 $\mu\mu$ were due to the necessity of an increased activation of 5 kg.-cals., the relative γ value at room temperature would be far less than 0·3. In fact, and although the matter has not been directly proved experimentally, it is very probable that the high temperature coefficieut in question is due, not to any extra activation subsequent to light absorption, but merely to an increase in the extinction of the chlorine, a suggestion first considered in detail by Wulf (*Proc. Nat. Acad. Sci.*, 1930, **16**, 27).

Until recently, there was no evidence to show whether any appreciable part of the very weak absorption in the chlorine banded spectral region was continuous. Jones and Spooner (*Trans. Faraday Soc.*, 1935, **31**, 811) have, however, demonstrated that, at numerous points between 504 and 532 $\mu\mu$, apparently free from lines, there is very definite absorption, the extinction coefficients being of the same magnitude as those found in the same region by von Halban and Siedentopf (*loc. cit.*), using a method which did not separate the effects of bands and of continuum. Although Jones and Spooner do not exclude the possibility of the presence in these regions of a large number of close unresolved lines, yet it seems likely that the absorption is mainly continuous.* This being the case, and although the measurements in question have not been extended as far as 546·1 $\mu\mu$, we shall assume that the primary process at this wave-length, and in the banded region generally, is optical dissociation to chlorine atoms, the absorbing chlorine molecules being of course

* We are much indebted to Dr. A. Elliott, of the University of Sheffield, for having kindly initiated these experiments.

in higher vibrating levels of the normal state. The difference, ΔE, of 4·3—5·0 kg.-cals. between the activation energies at 436 $\mu\mu$ and 546 $\mu\mu$, as calculated from the respective temperature coefficients, is due to an "activation energy" of the absorption process, and corresponds to the average energy difference between the actual absorbing molecules and those in the lowest vibrational quantum state. The differences in level between these higher states and $v'' < 0$ are as follows :

v''	1	2	3	4	5
Wave-number, cm.$^{-1}$	557	1106	1647	2180	2706
Kg.-cals.	1·58	3·14	4·68	6·19	7·69

The found value for ΔE suggests, therefore, that the absorbing molecules are those in which v'' is either 3 or 4, and chiefly the former. It is plain that in neither case will the energy content of these molecules, after absorption at 546·1 $\mu\mu$, permit of dissociation into $^2P_{1/2}$ and $^2P_{3/2}$ atoms (59·4 kg.-cals.). But clearly, all such molecules with $v'' = 4$, as also molecules with $v'' = 3$, assuming a slight contribution of 0·1—0·2 kg.-cals. of rotational energy, are potentially capable of giving two $^2P_{3/2}$ atoms (56·8 kg.-cals.).

According to Mulliken (*Physical Rev.*, 1930, **36**, 1440), chlorine, as also the other halogens, in addition to its known O_u^+ upper state, should also have three other associated upper states, components of a $^3\Pi$ multiplet, all with small D values (one of them repulsive), converging to a limit at 20,000 cm.$^{-1}$, and hence dissociating into two $^2P_{3/2}$ atoms. In the case of iodine, the infra-red band absorption system discovered by Brown (*ibid.*, 1931, **38**, 1187) is very possibly associated with transition from the normal state to one of these upper states, and a similar direct transition into the continuum of one of these states may perhaps be taking place in the case we are considering, with the result that chlorine atoms will be produced by absorptiou at 546·1 $\mu\mu$. In addition, however, an excited molecule in the O_u^+ state will have a certain probability of transition, by a predissociation process, into one of these $^3\Pi_u$ states, and this is the interpretation of our results which we prefer (cf., for iodine, van Vleck, *ibid.*, 1932, **40**, 544). A mechanism of this sort appears preferable to one involving collision between excited chlorine and other molecules. If the latter were correct, the relative γ value for 546 $\mu\mu$ should decrease rapidly when the total pressure is lowered below a certain low limit. It would be very difficult to test this point experimentally. We found γ to be much the same at $p = 47$ mm. as at $p = 1$ atm., *viz.*, 0·3. Presumably this figure measures the probability of the $O_u^+ \longrightarrow {}^3\Pi_u$ transition referred to. Less likely possibilities are that it depends on the probability that the absorption of 546·1 $\mu\mu$ light will raise normal chlorine molecules with $v'' = 3$ to the energy level of 56·8 kg.-cals., or that it depends on a difference of reactivity towards hydrogen molecules of excited and normal chlorine atoms.

It will have been noted that the agreement between Expts. 102 and 104 (Table III) is defective. On the basis of the above discussion, and on the assumption that Expts. 98—101 are sound, the result given by Expt. 104 is to be preferred, although a value of E_{436} of 5·0 kg.-cals. (temp. coeff. for 17—27° = 1·336) would be in conformity with the suggestions put forward; E is, of course, a composite figure, corresponding to the complex nature of the reaction under study.

Wave-length and Quantum Sensitivity.—The data from Part III plotted in Figs. 1 and 2 show that, as the wave-length of the exciting light decreases from 546·1 $\mu\mu$, γ (relative) increases and reaches unity at about 490 $\mu\mu$, a point still inside the banded spectrum region, but corresponding to 58·0 kg.-cals. per mol., a value sufficient to dissociate the absorbing molecule into two normal atoms. The steady rise of quantum efficiency we interpret as due to an increasing probability of spontaneous formation of two $^2P_{3/2}$ atoms from the excited O_u^+ state. We should expect to find a progressive decrease in temperature coefficient in the same region. In the temperature range 27—45°, Hertel (*Z. physikal. Chem.*, 1932, *B*, **15**, 325) found 1·48 for 480—515 $\mu\mu$, as compared with 1·37 for 400—480 $\mu\mu$. The value of ΔE derived from these figures, about 1·50 kg.-cals., is rather less than that corresponding to $v'' = 1$, *viz.*, 1·58 kg.-cals.; these molecules in turn would require to absorb at 515 $\mu\mu$ in order that they might be raised to the level of 56·8 kg.-cals./mol.

Further inspection of Figs. 1 and 2 shows γ (relative) to remain constant within experi-

mental error, at all events as far as 400 $\mu\mu$. Below this wave-length, values are only available for light of the mercury lines at 366, 334, 313, 303, 265, and 254 $\mu\mu$, the gap between 400 and 366 $\mu\mu$ being particularly unfortunate. The diagrams show, however, that although, with oxygen-free gases and a chlorine pressure of 45·7 mm., the quantum efficiency is not affected, or only doubtfully so (see discussion following Table VI), by increase in frequency over this wave-length range, yet it falls off appreciably in the two cases of (i) $p_{Cl_2} = p_{H_2} = 0{\cdot}5$ atm., oxygen present; and (ii) $p_{Cl_2} = 1{\cdot}7$ mm., $p_{H_2} = 0{\cdot}2$ mm., oxygen absent; the average value of γ (relative) being less than 0·8 and 0·7 respectively. In the latter case, a single comparison using $p_{Cl_2} = 0{\cdot}11$ mm. gave $\gamma_{313} = 0{\cdot}86$, whereas it was 0·65 at $p_{Cl_2} = 1{\cdot}7$ mm.

A change in frequency in the continuous-spectrum region can only affect the properties of the primary products of reaction, *i.e.*, the chlorine atoms. The higher the frequency, the greater will be their relative kinetic energies at the moment of separation. There is every reason to suppose that the reaction probability between colliding chlorine atoms and hydrogen molecules will be greater, rather than less, the higher their relative kinetic energy of approach. Nor will the course of the normal reaction chain depend appreciably, one way or the other, on the high velocity of the chlorine atom which initiates it. The only way in which the high frequency of the light can shorten the chain length appears to be by providing the activation energy required for the production of some substance, the formation of which reduces the concentration of the chain carriers (hydrogen or chlorine atoms) in the reacting system. After considering various possibilities, we put forward the following suggestions. The wave-lengths 478·5, 400, and 366 $\mu\mu$ correspond respectively to absorbed energy quantities of 59·4, 69·4, and 77·6 kg.-cals./mol. The average molar kinetic energies of separation of chlorine atoms produced at 400 $\mu\mu$ will be then 5 kg.-cals., and at 366 $\mu\mu$, 9·1 kg.-cals. The activation energy of the assumed process will lie between these limits.

We think that in the case of the experiments with 1·7 mm. of chlorine and low pressures of hydrogen set out in Tables IV and V, the effect observed is due to the reaction $Cl + Cl_2 \longrightarrow Cl_3$, taking place when the collision involves a chlorine atom of sufficiently high kinetic energy. The conditions of formation of Cl_3 radicals have recently been studied theoretically by Rollefson and Eyring (*J. Amer. Chem. Soc.*, 1932, **54**, 170). They conclude that the above reaction requires an activation energy with maximum and most probable values of 8·6 and 4·5 kg.-cals./mol. respectively, that this activation energy is entirely translational in nature, and that the quasi-molecule Cl_3' (the reaction $Cl + Cl_2 \longrightarrow Cl_3$ is probably exothermic), when once produced, will have a relatively long life, the above equation expressing this fact by not postulating the necessity of a three-body collision. As the ratio p_{H_2}/p_{Cl_2} in the present case is of the order of 0·1, it follows that, with light of sufficiently short wave-length, the result of the primary reaction is, to a great extent, the formation of two Cl_3 radicals rather than two Cl atoms. In these experiments, moreover, the chains are almost entirely broken on the walls (adsorption of chlorine atoms and recombination to molecular chlorine). A consideration of our quantum yields at the lowest pressure used, combined with calculations of collision numbers and of rates of diffusion of chlorine atoms to the walls of the reaction vessel, shows (details in a subsequent paper) that the efficiency of the latter in removing chlorine atoms from the reaction zone is very low, in agreement with the observations of Rodebush and Klingelhoefer (*J. Amer. Chem. Soc.*, 1933, **55**, 130) and of Schwab and Friess (*Z. Elektrochem.*, 1933, **39**, 586). It is natural to suppose that Cl_3 radicals are adsorbed more readily than Cl atoms and, as in these experiments they will have been present in concentrations far above the equilibrium value, a shorter chain length will be the result. Combined with this is the further fact that the efficiency of Cl_3–H_2 collisions is very probably less than that of Cl–H_2 collisions. According to Kimball and Eyring (*J. Amer. Chem. Soc.*, 1932, **54**, 3876), this ratio is as low as 10^{-3}—10^{-4}, whereas Rollefson (*J. Amer. Chem. Soc*, 1934, **56**, 579) puts it at 10^{-1}—10^{-2}. In any case, under the low pressure conditions prevailing in the experiments under discussion, even the latter disparity would be of importance, and the combination of the two factors we believe fully adequate to explain our results. The smaller effect found at $p_{Cl_2} = 0{\cdot}11$ mm. is to be anticipated in view of the larger proportion of photo-dissoci-

ated chlorine atoms which undergo their first collision after formation with hydrogen rather than with chlorine molecules.

The above interpretation of the experiments assumes a higher ratio $[Cl_3]/[Cl]$ than corresponds to the equilibrium $Cl_2 + Cl \leftrightarrow Cl_3$. The higher the total pressure, the more rapidly will equilibrium conditions be set up by molecular collisions, and the less important will be the rôle of the walls in terminating chains; consequently, the less likely will be any effect of wave-length on quantum efficiency. This we believe to be the reason for the difference between the results in Table VI as compared with those in Tables IV and V. Light of short wave-length will, as before, result in the formation of Cl_3 radicals, but for the reasons just given there will be no measurable effect on the quantum efficiency.

From what has been said, the proposed mechanism clearly cannot be responsible for the effects found with electrolytic gas at atmospheric pressure. This gas contains oxygen, and we suggest tentatively that the processes responsible for the decreased value of γ in short wave-length light (a rather smaller decrease than that just discussed) may be reactions of the type $Cl' + O_2 \longrightarrow ClO_2$, $Cl_3' + O_2 \longrightarrow Cl_2 + ClO_2$, the high translational energy of primarily formed chlorine atoms again supplying the necessary activation. The powerful inhibiting effect of ClO_2, most probably by the way of $ClO_2 + H \longrightarrow HCl + O_2$, is of course well known. Further examination of this suggestion reveals difficulties. Quite apart from questions of magnitude and nature of activation energy, the absolute quantum efficiencies measured in Part III are believed to have been only one-tenth of those obtained in Part II, respectively of the order of 10^4 and 10^5. The main chain-breaking reaction in both cases was the same ($H + H_2 + O_2 \longrightarrow$ products), indicating that the oxygen pressure was about ten times as high in the former as in the latter experiments. But the relative lowering of γ brought about by ultra-violet light was about the same in both cases. It is of course possible, but not very likely, that the estimate of absolute quantum efficiency in Part II (filtered light used) was seriously in error. We are not now in a position to test this point, and in the circumstances will not discuss the matter further, beyond remarking that calculations indicate that, if the reaction $Cl' + O_2 \longrightarrow ClO_2$ is solely responsible for the effect, the Cl′ atom must still be capable of reacting in this sense after at least 30 collisions with other molecules in the gaseous mixture. If $Cl_3 + O_2 \longrightarrow Cl_2 + ClO_2$ is responsible (the reaction would probably have a slight positive heat effect), then the conditions are, quite generally, more favourable to the suggestion.

Experiments in Presence of Oxygen.—We have left for discussion two points. The first is that, although 0·1 mm. of oxygen does not retard the reaction if the hydrogen pressure is of the order of 0·1 mm., yet a very marked retardation is observed at hydrogen pressures of the order of 0·01 mm. Although the accurate determination of small hydrogen pressures in presence of excess of oxygen is liable to appreciable error, we nevertheless think the effect a real one. The second point is that although at the higher pressures of hydrogen mentioned, oxygen does not retard reaction, yet some of it is found to have disappeared when, after the end of the experiment, all hydrogen present has been insolated away. It is of course possible that this oxygen consumption merely took place during the last stages of this final insolation, *i.e.*, when p_{H_2} had fallen to less than 0·01 mm., and the oxygen retardation referred to above had set in. Assuming, however, oxygen to have been consumed over the whole of our pressure range, we suggest the following explanation:

The primary process at all pressures of hydrogen is the union of hydrogen atoms and oxygen molecules:

$$(a)\quad H + O_2 \longrightarrow HO_2 + 40 \text{ kg.-cals.}$$

Reaction between this radical and hydrogen molecules can be conceived of as taking place in two ways, *viz.*,

$$(b)\quad HO_2 + H_2 \longrightarrow H_2O + OH + 63 \text{ kg.-cals.}$$
$$(c)\quad HO_2 + H_2 \longrightarrow H_2O_2 + H - 2 \text{ kg.-cals.}$$

Although (*b*) is highly exothermic, we suggest that it will at ordinary temperatures take place much less readily than (*c*), owing to its higher activation energy. This results

from the necessity of breaking both an O–O and an H–H linkage, whereas in (*c*) the latter only must be broken. On the other hand, it will take place more readily than (*c*), owing to its greater exothermicity, when H–O_2–H_2 triple collisions occur, the result of such collisions being

$$(d)\quad H + O_2 + H_2 \longrightarrow H_2O + OH + 103 \text{ kg.-cals.}$$

Both Chapman and Watkins (J., 1933, 743) and Norrish and Ritchie (*Proc. Roy. Soc.*, 1933, *A*, **140**, 713) ascribe the retarding effect of oxygen at high hydrogen pressures to reaction (*d*), and in all probability it was responsible for the large consumption of oxygen in our Expt. 72 (Cl_2 = 166 mm.; initial H_2 = 154 mm.).

At the lower hydrogen pressures used in our other experiments, triple collisions became very rare events. Such reactions as

$$HO_2 + Cl_2 \longrightarrow OH + Cl_2O - 15 \text{ kg.-cals.}$$
$$HO_2 + Cl_2 \longrightarrow HClO + ClO - 8{\cdot}5 \text{ kg.-cals.}$$
$$HO_2 + HCl \longrightarrow H_2O + ClO + 7{\cdot}5 \text{ kg.-cals.}$$

we imagine to be excluded in practice; apart from the endothermicity of the first two, all would have high activation energies. The HO_2 radicals will rather react in accordance with (*c*); and this reaction, with the regeneration of a hydrogen atom, will correspond to our observations, *i.e.*, consumption of oxygen without inhibition of hydrogen chloride formation. Finally, as the hydrogen pressure falls still further, reaction (*c*) will become unimportant compared with (*e*) $HO_2 \longrightarrow H_2O_2$, H_2O, O_2, occurring either on the walls or in the gas phase, and consumption of oxygen will again be accompanied by retardation of the main reaction.

In the absence of more experiments, we shall not discuss the above suggestions any further, beyond mentioning that they may be relevant in connexion with the somewhat discordant experimental results obtained during the study of the photochemistry of hydrogen–oxygen mixtures (Hinshelwood and Williamson, "Reaction between Hydrogen and Oxygen," Chapter III, 1934). They would point to low total pressures and temperatures as favouring the formation of hydrogen peroxide, and high total pressures and temperatures that of water.

SUMMARY.

(1) Experiments with carefully monochromatised light confirm the earlier conclusion that a hydrogen–chlorine mixture will react in light of wave-length 546 μμ. On the other hand, negative results were obtained at 579 μμ.

(2) Comparative measurements of the temperature coefficient of the reaction at 436 μμ and 546 μμ have been carried out.

(3) In gas mixtures free from oxygen and of about 2 mm. total pressure, the relative quantum efficiency is found to be lower in ultra-violet than in visible light. At higher pressures no such difference was observed.

(4) At hydrogen pressures of 0·01—0·5 mm., the presence of 0·1 mm. of oxygen does not retard the reaction although oxygen appears to be consumed. Evidence was obtained of a marked retardation when the hydrogen pressure fell below 0·01 mm.

(5) The above results are discussed and explanations proposed. In connexion with (1) and (2), it is suggested that active light absorption in the green is connected with the continuous background of the banded spectrum region, and that the reaction mechanism is essentially the same as when absorption takes place in the continuum proper. The observations under (3) are explained on the basis of a mechanism involving the formation of Cl_3 radicals in light of short wave-length.

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53. *Free Radicals and Atoms in Primary Photochemical Processes. The Free* n-*Propyl Radical.*

By Thomas G. Pearson and Ronald H. Purcell.

Numerous attempts have been made to prepare higher homologues of methyl and ethyl. Paneth and Lautsch (*Ber.*, 1931, **64**, 2708) decomposed tetra-*n*-propyl-lead at about 400°, using the same method as had yielded free methyl and ethyl (Paneth and Hofeditz, *Ber.*, 1929, **62**, 1335), and investigated the action of the products on lead, antimony, and zinc. With lead, a yellow liquid resulted which decomposed above 100°, with separation of metallic lead and formation of minute amounts of liquid non-volatile in a vacuum at the ordinary temperature. Antimony gave bisdimethylantimony, and zinc gave dimethylzinc with traces of what may have been a higher zinc alkyl. It was assumed, therefore, that any propyl produced decomposed rapidly to give methyl. It had been observed that above 600° ethyl decomposes completely to methyl (Paneth and Loleit, J., 1935, 369), but attempts to lower the decomposition temperature of tetrapropyl lead by the use of catalysts or high-frequency discharges were unsuccessful (*idem, ibid.*, p. 380). Rice (*Trans. Faraday Soc.*, 1934, **30**, 152) sought to carry the propyl radicals in a current of ethylene in an effort to inhibit the decomposition $CH_3{\cdot}CH_2{\cdot}CH_2 \longrightarrow CH_3 + C_2H_4$, but obtained only methyl, and concluded from this and other experiments that in thermal decomposition in the range 450—750° practically all radicals higher than ethyl dissociate to give olefins and methyl, ethyl, or atomic hydrogen.

On the other hand, Rice and Evering (*J. Amer. Chem. Soc.*, 1933, **55**, 3898) passed a mixture of azo*iso*propane and acetone through a silica tube heated at 450—550°, and measured the life of active fragments in the effluent gases. The curve obtained by plotting concentration of radicals against distance from the heated zone was compared with that from tetramethyl-lead under identical conditions. The curves coincided exactly up to 20 cm.; beyond, the concentration did not diminish so rapidly with azo*iso*propane as with tetramethyl-lead, indicating the presence of an active fragment of comparatively long life.

Since methyl and ethyl had been isolated in the photodissociation of acetone and diethyl ketone respectively (Pearson and Purcell, J., 1934, 1718; 1935, 1151; Terenin, *Trans. Faraday Soc.*, 1935, **31**, 1483), it was thought that propyl should result from similar experiments with di-*n*-propyl ketone, and this expectation was encouraged by the work of Bamford and Norrish (*Chem. and Ind.*, 1935, **54**, 488; J., 1935, 1504), who, from the chemical and spectroscopic analysis of the photolysis, concluded that at least a proportion of the ketone decomposes to yield propyl radicals.

It is now shown that when di-*n*-propyl ketone is irradiated with ultra-violet light, it dissociates to form free *n*-propyl radicals. The ketone was allowed to stream at a pressure of about 2 mm. Hg through a quartz tube covered to exclude light except for a 10-cm. length which was irradiated with a quartz mercury-vapour arc. Active fragments were detected 35 cm. (the maximum available distance) from the irradiated zone by their removal of metallic mirrors. Whereas the reaction with arsenic, antimony, or tellurium might be ascribed to atomic hydrogen, that with lead precludes this possibility (Pearson, Robinson, and Stoddart, *Proc. Roy. Soc.*, 1933, **142**, 275), and limits the fragments to an organic free radical. Small quantities of the propyl derivatives of arsenic, antimony, tellurium, and lead are not readily identified. We therefore used mercury (Rice, Johnson, and Evering, *J. Amer. Chem. Soc.*, 1932, **54**, 3529; 1934, **56**, 2105), realising that the results must be interpreted with caution (J., 1935, 1151). In the present instance, we avoided exciting the mercury by irradiating with hot mercury arcs, and in subsequent experiments, as a further precaution, filtered the light through a layer of mercury vapour sufficiently thick to ensure the absence of resonance radiation. Under these conditions the products of the photolysis reacted with mercury to form an evil-smelling, colourless liquid which reacted with mercuric bromide to form crystalline plates of *n*-propylmercury bromide. No other alkylmercury bromide was revealed by the fractional sublimation of

the reaction products. Hence the radical responsible for the removal of the arsenic, antimony, tellurium, and lead mirrors must have been *n*-propyl, the half-life period of which at the room temperature in a silica tube of 8-mm. diam. was found to be $2{\cdot}3 \times 10^{-3}$ sec., compared with $3{\cdot}3 \times 10^{-3}$ and $5{\cdot}3 \times 10^{-3}$ sec. for ethyl and methyl respectively (Paneth, Hofeditz, and Wunsch, J., 1935, 375; *Ber.*, 1929, **62**, 1335; Paneth and Lautsch, *loc. cit.*; Pearson, J., 1934, 1721).

It may be pointed out that a life period determined at the room temperature is no criterion of thermal stability, and the failure of earlier workers to obtain the propyl radical by the thermal decomposition of compounds is not irreconcilable with our results.

Experimental.

Di-*n*-propyl ketone (250 g.) was dried over calcium chloride, and distilled at atmospheric pressure through a 70-cm. bead column, the middle fraction (100 g.), b. p. 142—143°, being collected. Mercury was purified with nitric acid, dried, and redistilled in a vacuum. Commercially pure mercuric bromide was recrystallised from water.

Fig. 1.

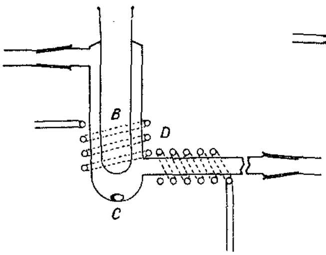
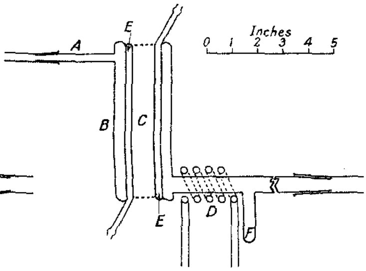


Fig. 2.



The apparatus employed for the experiments with solid metals was identical with that previously described (J., 1935, 1153). Butyl phthalate was used in the manometers to avoid the presence of mercury in the apparatus. Mirrors of arsenic, antimony, or tellurium, 2 mm. wide and dense enough to be dark brown, situated 15 cm. from the nearer edge of the irradiated zone, were removed completely in about one hour. The products condensed in the liquid-air trap were always colourless and smelled of the original ketone. The absence of the typical odour of dimethyl or diethyl telluride was noteworthy. Lead mirrors of a similar density were removed in comparable, but slightly longer, times. Mirrors were unattacked in the absence of ultra-violet light.

The radicals were identified by their reaction with mercury. In the earlier experiments (*Fig. 1*), the ketone streamed at about 2 mm. Hg through the transparent silica tube (12 mm. diam.) wherein it was irradiated by a cold arc (Thermal Syndicate, T/M5/249) and a hot arc (T/M5/254) burning on opposite sides of the tube. The products of the photolysis and excess of ketone impinged on mercury on the surface of the condenser *B*. The mercury was constantly refreshed from the pool *C* by heating with a micro-burner. In order to restrict the mercury to the immediate neighbourhood of *B*, the outside of the quartz vessel and 10 cm. of the tube were surrounded by a cooling spiral *D*. The products of the reaction with mercury and excess of ketone condensed in a liquid-air trap, and, by manipulation of taps provided in the system, could be distilled on to a small quantity of mercuric bromide with which mercury-alkyls form comparatively non-volatile alkylmercury bromides. The ketone was then re-admitted to the quartz tube, and the operations repeated. During the whole of the processes, precautions were taken to avoid the presence of mercury in the irradiated zone, and, provided it was not there to start with, the rate of streaming was sufficient to prevent diffusion against the gas stream during irradiation. Fractional sublimation of the alkylmercury bromides from four

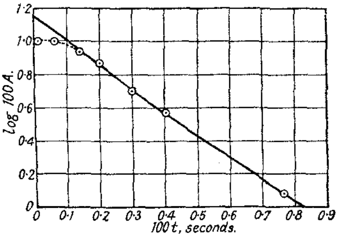
runs yielded five fractions. The first three, m. p. 136—138°, were laminated plates which began to recrystallise at 120° to form clusters of curiously curved needles, the typical appearance and behaviour of *n*-propylmercury bromide. The m. p., 136—138°, of an authentic specimen of mercuric bromide was not depressed by admixture with an equal part of the fourth fraction. The fifth fraction was the highly polarising rhombs of mercuric bromide, which sublimed from the cover-slips at 230°.

In a second experiment, the 12-mm. silica tube was replaced by one of 5-mm. diameter in order further to restrict the diffusion of mercury. To reduce the likelihood of excitation, only the hot arc was used for irradiation. All the fractions obtained melted between 136° and 138°, and from their appearance were *n*-propylmercury bromide. In an endeavour to detect other alkylmercury bromides which might have been present, the products (0·2 g.) from seven runs were collected. On sublimation, isotropic polygonal grains were obtained, m. p. 122—130°, which began at 100° to be transformed into cruciform tablets of unique appearance. This substance was unlike any individual alkylmercury bromide, or mixture of alkylmercury bromides (HgMeBr, m. p. 160—164°; HgEtBr, m. p. 193·5°; $HgPr^{a}Br$, m. p. 136—138°; $HgPr^{\beta}Br$, m. p. 98°). It was found, however, that a mixture of mercuric bromide, *n*-propylmercury bromide, and di-*n*-propyl ketone, when evaporated to dryness and sublimed, yielded crystals that behave in an identical fashion. The same product was obtained from the first two compounds, but not from either of the others of the three possible binary mixtures. Later sublimates from the photochemical experiments melted at 136—138°, and admixture with authentic *n*-propylmercury bromide did not depress the m. p. of representative fractions.

Sublimation of the products from blank experiments in the absence of ultra-violet light yielded only mercuric bromide.

Since we had detected alkyl radicals by their action on arsenic, antimony, tellurium, and lead in the complete absence of mercury, whilst with mercury only propyl was detected, it was clear that unless the whole photodissociation had changed its course in the presence of mercury vapour—which might, in spite of the precaution, have diffused into the irradiated zone—then the existence of the propyl radical was established.

Fig. 3.



In order finally to rule out the excitation of mercury as the cause of the *n*-propylmercury bromide and to improve the yields, we used the transparent silica apparatus shown in Fig. 2. The ketone was admitted at *A* to the outer annulus *B*, wherein it was irradiated by a vertical arc in *C*, and streamed over a film of mercury on the surface of the silica tube which was kept cold by a metal water-jacket *D*. The mercury surface was periodically renewed by warming the reservoir *F*. The outer surface of *B* was silvered. In preliminary experiments, the annulus *E*, which was evacuated, contained a little mercury. Unfortunately, the heat generated by the arc raised the temperature of the apparatus to about 300°, and it was impossible to estimate how far this might influence the dissociation, so the experiment was interrupted after an hour. The products condensed in the liquid-air trap were treated with mercuric bromide and sublimed into two fractions, the second of which proved to be mercuric bromide. The first consisted of isotropic polygonal grains, which became cruciform at 100—110° and melted at 122—130°, identical with the addition compound of *n*-propylmercury bromide and mercuric bromide.

In the final experiments, we streamed cold water through the annulus *E*, and passed the lamp through accurately fitting rings which closed the inner tube and served to contain the mercury. A stream of coal-gas protected the mercury from oxidation. An asbestos screen round the lower portion of the inner mercury lamp prevented the direct irradiation of the ketone in the horizontal tube. The resonance line was absent in a photograph of the spectrum taken through a slit in the silvering. The products from five runs were treated with mercuric bromide and sublimed into fifty fractions, the earlier of which were identical with the addition compound of *n*-propylmercury bromide and di-*n*-propyl ketone, and the later gave a series of m. p.'s approaching that of pure *n*-propylmercury bromide until sublimation was interrupted on the appearance of mercuric bromide. Again, no evidence of other alkylmercury bromides was obtained. It is therefore concluded that the alkylmercury bromide did not result by the action

of excited mercury atoms on the ketone, but by the action of free *n*-propyl radicals on metal mercury.

The half-life period of the fragments, measured by comparing the rates of removal of standa mirrors in the usual way (J., 1934, 1721), was $2{\cdot}3 \times 10^{-3}$ sec. The results are shown in Fig. wherein the ordinates are the logarithms of the reciprocals of the times of removal of the mirro (A), and the abscissæ are the times (t) taken for the radicals to reach the mirrors.

SUMMARY.

The *n*-propyl radical of half-life period $2{\cdot}3 \times 10^{-3}$ sec. is formed during the phot dissociation of di-*n*-propyl ketone in ultra-violet light, and has been detected by its actic on arsenic, antimony, tellurium, and lead, and identified through conversion into : propylmercury bromide with precautions to exclude the excitation of the mercury used : identification.

The authors thank Mr. H. H. Glazebrook for his assistance in some of the experiment and the Royal Society for a grant which assisted the purchase of apparatus.

IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, December 23rd*, 1935.]

54. *Reactions of* o-*Hydroxybenzylidenediacetophenones. Part VI. Diacetophenones derived from 3-Methoxysalicylaldehyde.*

By G. H. BEAVEN and DOUGLAS W. HILL.

THE investigation of the reactions of *o*-hydroxybenzylidenediacetophenones derive from salicylaldehyde and its 4- and 5-methoxy-derivatives (J., 1934, 1255; 1935, 85) ha been extended to derivatives of 3-methoxysalicylaldehyde. Acetophenone, *p*-methox acetophenone, and *p*-methylacetophenone were each condensed with 3-methoxysalicy aldehyde in alcoholic solution under the influence of concentrated sodium hydroxic solution to give 3-*methoxysalicylidene-diacetophenone*, -*di*-(p-*methoxyacetophenone*), an -*di*-(p-*methylacetophenone*) respectively. In each case the corresponding 3-*methox chalkone* also was isolated. The separation of the diketone from the sodium salt of t chalkone was a tedious operation, owing to the sparing solubility of the latter in water

The diketones were converted by boiling glacial acetic acid into the correspondi substituted 4-*phenacylideneflavenes*, which, contrary to previous experience, crystallis from the cold reaction mixtures. So readily were the latter compounds formed that tl 4-*phenacylflavenes* were obtained only with great difficulty and in small yields. In : attempt to effect ring closure without conversion into 4-phenacylidene derivatives, recour was had to non-acidic reagents: anhydrous sodium sulphate (compare Baker and Walke J., 1935, 646) was without effect, and treatment of 3-methoxysalicylidenedi-(*p*-methy acetophenone) with acetic anhydride in place of acetic acid led to 2-*acetoxy-3-methox benzylidenedi*-(p-*methylacetophenone*). Simple flavylium salts were obtained from tl diketones on treatment in cold glacial acetic acid with dry hydrogen chloride in the mann previously described and substituted 4-*phenacylflavylium* salts were similarly prepare without difficulty from the 4-phenacylideneflavenes.

The diketones of salicylaldehyde and its 4- and 5-methoxy-derivatives resemble or another closely in behaviour, but differ considerably from the derivatives of 3-methox salicylaldehyde, most markedly in ease of formation and purification and in the difficult of obtaining the 4-phenacyl derivatives. The divergence in behaviour of derivatives (3- and of 4-methoxysalicylaldehyde has been commented upon by Robinson (J., 192 **125**, 207).

EXPERIMENTAL.

3-*Methoxysalicylidenediacetophenone*.—A solution of 3-methoxysalicyladehyde (15 g.) an acetophenone (25 g.) in alcohol (120 c.c.) was treated with a hot solution of sodium hydroxic (30 g. in 30 c.c. of water). The resulting deep red solution was heated on the water-bath fc

1 hour, kept over-night, poured into water (5 l.), and heated to dissolve as much as possible of the sparingly soluble sodium salt of the chalkone formed as a by-product. The insoluble portion was filtered off and fractionally crystallised from alcohol, the *diketone* being obtained as colourless sandy crystals (10 g.), m. p. 145—146° (Found: C, 76·5; H, 5·9. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%). The aqueous mother-liquor on acidification yielded 3-methoxychalkone, which separated from alcohol in yellow prisms, m. p. 112° (Robinson, J., 1924, **125**, 207, gives m. p. 112°).

3-*Methoxysalicylidenedi*-(p-*methoxyacetophenone*).—In the same manner this diketone was prepared from the aldehyde (10 g.) and *p*-methoxyacetophenone (20 g.). After the reaction mixture had been poured into water, the solution was heated on the steam-bath with acetic acid, and the resulting mixture of chalkone and diketone fractionally crystallised from alcohol. The *diketone* separated in colourless plates (4·0 g.), m. p. 163—164° (Found: C, 71·8; H, 6·1. $C_{26}H_{26}O_6$ requires C, 71·9; H, 6·0%). 3 : 4′-*Dimethoxychalkone* was obtained from the alcohol in bright yellow plates, m. p. 142° (Found: C, 71·6; H, 5·7. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%).

3-*Methoxysalicylidenedi*-(p-*methylacetophenone*).—This compound was prepared from the aldehyde (10 g.) and *p*-methylacetophenone (18 g.) in the above-described manner. The product was extracted with benzene after the pouring into water, and the benzene-soluble portion crystallised from alcohol, giving soft colourless needles (4·0 g.), m. p. 112° (Found: C, 77·7; H, 6·5. $C_{26}H_{26}O_4$ requires C, 77·6; H, 6·5%). The aqueous mother-liquor yielded on acidification 3-*methoxy*-4′-*methylchalkone*, which separated from alcohol in hard yellow needles, m. p. 131° (Found: C, 76·0; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%).

8-*Methoxy*-4-*phenacylideneflavene*.—3-Methoxysalicylidenediacetophenone (4 g.) was refluxed in glacial acetic acid (25 c.c.) for 1 hour. On cooling, the sparingly soluble *product* crystallised; recrystallised from alcohol, it formed bright yellow needles (1·5 g.), m. p. 192° (Found: C, 81·1; H, 5·3. $C_{24}H_{18}O_3$ requires C, 81·4; H, 5·1%).

8-*Methoxy*-4-*phenacylflavene*.—The same diketone (2 g.) was refluxed for 10 minutes with glacial acetic acid (30 c.c.), the solution poured into water (500 c.c.), and the yellow precipitate collected and crystallised alternately from light petroleum (b. p. 60—80°) and alcohol, yielding finally almost colourless, fine needles (0·2 g.), m. p. 136—137° (Found: C, 80·7; H, 5·7. $C_{24}H_{20}O_3$ requires C, 80·9; H, 5·6%).

8-*Methoxyflavylium Ferrichloride*.—Dry hydrogen chloride was passed for 5 minutes through a suspension of 3-methoxysalicylidenediacetophenone (1 g.) in acetic acid (10 c.c.), and the resulting clear reddish-brown solution treated with ferric chloride (0·5 g. in 7 c.c. of acetic acid). The rosettes of reddish-brown needles that separated were crystallised from glacial acetic acid; m. p. 162° (yield, 0·5 g.) (Found: Fe, 12·7. Calc. for $C_{16}H_{13}O_2Cl_4Fe$: Fe, 12·9%). Robinson (*J.*, *1924*, **125**, 209) gives m. p. 157°.

8-*Methoxy*-4-*phenacylflavylium Ferrichloride*.—In a similar way, from a cooled suspension of 8-methoxy-4-phenacylideneflavene (0·75 g.) in glacial acetic acid (8 c.c.) (dry hydrogen chloride passed for 5 minutes; then ferric chloride, 0·4 g., in acetic acid, 4 c.c., added), a precipitate was obtained, which was washed with ether and recrystallised from acetic acid, forming bronze-coloured needles (0·7 g.), m. p. 197—198° (Found: C, 52·1; H, 3·5; Fe, 10·0; Cl, 27·1. $C_{24}H_{19}O_3Cl_4Fe$ requires C, 52·1; H, 3·4; Fe, 10·1; Cl, 25·7%).

8 : 4′-*Dimethoxy*-4-(p-*methoxyphenacylidene*)*flavene*.—3-Methoxysalicylidenedi-(*p*-methoxyacetophenone) (2 g.) was refluxed with glacial acetic acid (15 c.c.) for 1 hour. On cooling, the *product* separated in yellow needles; after twice crystallising from alcohol, it had m. p. 195° (yield, 0·7 g.) (Found: C, 75·0; H, 5·3. $C_{26}H_{22}O_5$ requires C, 75·3; H, 5·3%).

8 : 4′-*Dimethoxyflavylium Ferrichloride*.—The same diketone (0·75 g.) was suspended in glacial acetic acid (7·5 c.c.) and treated in the usual way with hydrogen chloride and ferric chloride. The product crystallised from glacial acetic acid in dark red needles (0·5 g.), m. p. 179° (Robinson, *loc. cit.*, gives m. p. 180°).

8 : 4′-*Dimethoxy*-4-(p-*methoxyphenacyl*)*flavylium Ferrichloride*.—8 : 4′-Dimethoxy-4-(*p*-methoxyphenacylidene)flavene (0·5 g.), suspended in glacial acetic acid (5 c.c.), was treated in the normal manner with hydrogen chloride and the sparingly soluble chloride which separated was filtered off rapidly, washed with dry ether, and transferred to hot glacial acetic acid. Ferric chloride (0·3 g.), dissolved in glacial acetic acid (3 c.c.), was added. The *ferrichloride* crystallised on cooling and was recrystallised from hot acetic acid, forming dark red plates with an intense purple glance (0·3 g.), m. p. 193° (Found: C, 50·8; H, 3·7; Fe, 9·1; Cl, 24·8. $C_{26}H_{23}O_5Cl_4Fe$ requires C, 50·9; H, 3·7; Fe, 9·1; Cl, 23·2%).

8-*Methoxy*-4-(p-*methylphenacylidene*)-4′-*methylflavene*.—3-Methoxysalicylidenedi-(*p*-methyl-

acetophenone) (1 g.) was refluxed in the usual way with acetic acid (20 c.c.). The product crystallised from alcohol in deep yellow needles (0·3 g.), m. p. 200° (Found: C, 81·4; H, 5·7. $C_{26}H_{22}O_3$ requires C, 81·7; H, 5·8%).

2-Acetoxy-3-methoxybenzylidenedi-(p-*methylacetophenone*).—The same diketone (0·5 g.) was refluxed with acetic anhydride (15 c.c.) for 30 minutes. After cooling, the pale yellow solution was poured into water (500 c.c.), and the precipitated solid removed after 12 hours. It separated from light petroleum (b. p. 60—80°) in hard colourless crystals (0·4 g.), m. p. 120° (Found: C, 75·6; H, 6·4. $C_{28}H_{28}O_5$ requires C, 75·7; H, 6·3%).

8-*Methoxy-4'-methylflavylium Ferrichloride.*—The above diketone (0·7 g.) in glacial acetic acid (7 c.c.) was treated in the usual manner with hydrogen chloride and ferric chloride. The resulting *ferrichloride* separated from glacial acetic acid in brown crystals (0·5 g.), m. p. 179° (decomp.) (Found: C, 45·6; H, 3·4; Fe, 12·3; Cl, 32·0. $C_{17}H_{15}O_2Cl_4Fe$ requires C, 45·4; H, 3·3; Fe, 12·5; Cl, 31·6%).

8-*Methoxy*-4-(p-*methylphenacyl*)-4'-*methylflavylium Ferrichloride.*—The corresponding phenacylideneflavene above (0·5 g.) was suspended in glacial acetic acid (5 c.c.) and converted into the *ferrichloride* in the usual manner. The latter crystallised from acetic acid in rosettes of orange-brown needles (0·3 g.), m. p. 192° (decomp.) (Found: C, 53·5; H, 4·0; Fe, 9·5; Cl, 24·6. $C_{26}H_{23}O_3Cl_4Fe$ requires C, 53·7; H, 4·0; Fe, 9·6; Cl, 24·4%).

The authors thank Dr. M. Nierenstein, in whose laboratory most of the work was carried out, and also the Colston Research Society of the University of Bristol for a grant.

THE UNIVERSITY, BRISTOL.
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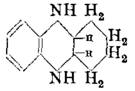
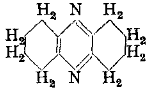
55. *The Phenazine Series. Part III. The Isomeric Octahydrophenazines.*

By G. R. CLEMO and H. McILWAIN.

IN preparing a considerable quantity of 1 : 2 : 3 : 4-tetrahydrophenazine (J., 1934, 1991), we isolated a small amount of an *octahydrophenazine*, m. p. 147°, as a by-product. We have recorded (J., 1935, 738) the production of a 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine, m. p. 156° (there given in error as 150°), by the sodium amalgam reduction of the tetrahydro-compound. The following results prove these two compounds to be geometrical and not structural isomerides: both are dehydrogenated smoothly to phenazine; both yield N-*nitroso*-compounds (m. p. 109° and 126°), from which it follows that the central heterocyclic ring is in each case reduced, as in (I); and both give the ferric chloride colour reactions characteristic of substituted *o*-phenylenediamines.

(I.) 

 (II.)

In addition, by the reduction of 1 : 2 : 3 : 4-tetrahydrophenazine by a nickel catalyst *A* made from nickel nitrate according to Gattermann ("Laboratory Methods of Organic Chemistry," English edition, 1934, p. 370), a third octahydrophenazine, m. p. 109°, is obtained, which also is dehydrogenated to phenazine, but yields no nitroso-compound or ferric chloride colour reaction. It is therefore the 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenazine (II) described by Wallach (*Annalen*, 1924, **437**, 177) and by Godchot (*Compt. rend.*, 1925, **180**, 444). On theoretical grounds, (II) would not be expected to exist in isomeric forms. The isomeric 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazines are, however, produced from the tetrahydro-compound by reduction with a nickel catalyst *B* prepared from nickel hydroxide (Rupe, *Helv. Chim. Acta*, 1918, **1**, 453); in the vapour phase at 180°, the main product is the compound of m. p. 156°, but in glacial acetic acid at room temperature the 147°-isomeride is produced. The actions of the two catalysts are different, for when either of the two compounds (I) is passed over catalyst *A* it is

converted into the isomeride (II); the latter is, however, recovered unchanged after passage over catalyst *B*. We do not know of any other case in which the use of the two catalysts has caused radically different reductions; it is noteworthy, however, that they are of different physical appearance.

Though the octahydrophenazine isolated as a by-product in the preparation of tetrahydrophenazine from *o*-phenylenediamine and *cyclo*hexane-1 : 2-dione is presumably produced on account of the reducing action of one or both of these reactants, it has not been found possible to reduce tetrahydrophenazine to the octahydro-compound by treating it with the diamine or the diketone under the conditions of the reaction (*loc. cit.*), which indicates that the reduction leading to the production of the octahydrophenazine must have occurred before or during the condensation.

In addition to the nickel reduction mentioned above, it is possible to reduce the tetrahydrophenazine almost quantitatively to the octahydrophenazine of m. p. 147° by means of palladium charcoal in glacial acetic acid. The following table summarises the various reduction results :

Initial material.	Reducing agent.	Product.
1 : 2 : 3 : 4-Tetrahydrophenazine	(*a*) Sodium–alcohol	1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydrophenazine, m. p. 156°
	(*b*) Pt or Pd; or Ni [from $Ni(OH)_2$] in glacial acetic acid	1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydrophenazine, m. p. 147°
	(*c*) Ni [from $Ni(NO_3)_2$] at 180°	1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-Octahydrophenazine
	(*d*) Ni [from $Ni(OH)_2$] at 180°	1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydrophenazine, m. p. 156°, with a little of its 147°-isomeride.
1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydrophenazine, m. p. 156°	(*a*) Sodium-alcohol; H_2 with Pd in acetic acid; Ni [from $Ni(OH)_2$] at 180°	No change
	(*b*) Ni [from $Ni(NO_3)_2$] at 180°	1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-Octahydrophenazine
1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydrophenazine, m. p. 147°	(*a*) Sodium–alcohol; H_2 with Pd in acetic acid	No change.
	(*b*) Ni [from $Ni(NO_3)_2$] at 180°	1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-Octahydrophenazine
	(*c*) Ni [from $Ni(OH)_2$] at 180°	Partly converted into 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine, m. p. 156°

The most suitable method of dehydrogenating the reduced phenazines described here has been found to be ½ hour's heating at 200° with palladium charcoal; it is much superior to the iodine method employed for the preparation of phenazine and its homologues from their 1 : 2 : 3 : 4-tetrahydro-forms (J., 1934, 1991) and to the zinc dust distillation used by Godchot (*loc. cit.*) for the conversion of a duododecahydrophenazine into phenazine.

It has not been found possible to interconvert the *cis-trans* forms of 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine by refluxing with glacial acetic acid, or sodium ethoxide, or by keeping their concentrated sulphuric acid solutions for considerable periods; but the 147°-isomeride is converted into the 156°-compound by passage in a hydrogen stream over catalyst *B*. With respect to the configurations of these two isomerides, their methods of production point to the 147°-compound being the *cis*- and the 156°-compound the *trans*-isomeride (compare Willstätter and Seitz, *Ber.*, 1924, **57**, 683; W. Hückel, *Annalen*, 1926, **451**, 109, 132). The latter should be resolvable into optically active forms.

It is hoped that the study, now in progress, of the fully reduced phenazines will afford further evidence on this question, and also add knowledge to the increasingly important question of the stereochemistry of polycylic compounds.

EXPERIMENTAL.

1 : 2 : 3 : 4 : 9 : 10 : 11 : *12-Octahydrophenazine, m. p.* 156° (see J., 1935, 738).—A much improved method is the following : To a solution of 1 : 2 : 3 : 4-tetrahydrophenazine (1·8 g.)

in absolute alcohol (75 c.c.) boiling under reflux, sodium (10 g.) was added gradually; the yellow solution became colourless, and when the reaction was complete it was poured into water (150 c.c.) and extracted with ether. The residue on removal of ether was repeatedly crystallised from alcohol, yielding the 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine in white needles (1·4 g.). The action of sodium in amyl-alcoholic solution was essentially the same, and a larger excess of sodium produced no different result.

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenazine, m. p.* 147°.—1 : 2 : 3 : 4-Tetrahydrophenazine (1 g.) in absolute alcohol (10 c.c.) with palladium charcoal (0·1 g.) was shaken vigorously for 20 hours in a hydrogen atmosphere of 100 lb. per sq. in. The catalyst was removed and when the filtrate was concentrated the bulk of the *octahydrophenazine* separated in colourless plates (0·9 g.), m. p. 147°, depressed to 122—124° by admixture with the 156°-isomeride (Found: C, 76·8; H, 8·8. $C_{12}H_{16}N_2$ requires C, 76·6; H, 8·5%).

Reduction of the same amount of tetrahydro-compound in glacial acetic acid (10 c.c.) with nickel catalyst *B* (1 g.) under the above conditions for 12 hours yielded the same product (0·8 g.). The same material (0·5 g.) was also obtained during the crystallisation of tetrahydrophenazine (40 g.) (*loc. cit.*) from light petroleum.

No molecular compound or complex salt was obtained between this octahydrophenazine and phenazine when examined by the methods previously described (J., 1935, 738).

Catalytic Reductions with Nickel.—The following method was devised for the reduction of small amounts of not very volatile materials. A slightly inclined, hard-glass tube, 16″ × ½″, contained a 10″ column of the catalyst, held between asbestos plugs and heated by a small gas furnace fitted with a thermometer. The material to be reduced was placed in a boat in the upper part of the tube and was driven over the catalyst in a stream of hydrogen by heating a gauze surrounding the tube at that point. The hydrogen (from zinc and hydrochloric acid) was washed in silver nitrate solution, alkaline permanganate solution, and concentrated sulphuric acid, and at the exit end of the tube it was passed through a trap containing alcohol.

The nickel catalyst *A* was prepared from the nitrate by the method of Gatterman (*loc. cit.*) and reduced at 300—310° for 2 hours, and catalyst *B* from nickel hydroxide by a 48 hours' reduction at 370—380° (Rupe, *loc. cit.*). The hydrogenations were performed at 175—185° and required about 6 hours. The catalyst (about 20 g.) was reduced in a hydrogen stream of 50 c.c. per minute while the gas was being actively absorbed; the rate was later diminished to 15 c.c. per minute. The hydrogenations were conducted in a stream of 40 c.c. per minute.

Hydrogenation of 1 : 2 : 3 : 4-*tetrahydrophenazine.* (i) *With catalyst* A. The compound (1 g.) was passed through the apparatus just described; extraction of the catalyst and crystallisation from dilute alcohol yielded an octahydrophenazine (0·5 g.), m. p. 109° (Found: C, 76·7; H, 8·55. Calc. for $C_{12}H_{16}N_2$: C, 76·6; H, 8·5%).

(ii) *With catalyst* B. The product from tetrahydrophenazine (1 g.), when crystallised from light petroleum, yielded 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine (0·4 g.), m. p. 156° (not depressed by admixture with the product of the sodium–alcohol reduction of the tetrahydro-compound), recovered tetrahydrophenazine (0·3 g.), and a fraction (0·2 g.), m. p. 122—124°, which on further laborious fractionation from light petroleum or, better, from benzene yielded some octahydrophenazine, m. p. 156°, though the bulk still melted at 123—124°. The analysis (Found: C, 77·0; H, 8·4. Calc. for $C_{12}H_{16}N_2$: C, 76·6; H, 8·5%) indicated that no further-reduced compound was present in the bulk; though we were unable to separate it completely, this probably consisted of mixed crystals of the two 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazines, for when these two compounds were crystallised together they yielded a fraction which after repeated crystallisation melted at 123—124°. A further passage of this material over the same catalyst enabled more of the 156°-isomeride to be obtained from it.

The action of hydrogen on the isomeric octahydrophenazines under the influence of catalysts A *and* B. (i) *Isomeride, m. p.* 156°, *with catalyst* A. The compound (1 g.), when passed once through the furnace, yielded 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenazine (0·5 g., from dilute alcohol), and 0·4 g. of the initial material was recovered. A more complete conversion was obtained on repassing the material under the same conditions.

(ii) *Isomeride, m. p.* 156°, *with catalyst* B. The bulk of the material was recovered unchanged, but a small fraction (0·1 g. from 2 g.) was obtained, m. p. 120—124°, which proved to be a mixture of the type described above.

(iii) *Isomeride, m. p.* 147°, *with catalyst* A. The product from the passage of 1 g. was crystallised from alcohol and yielded recovered material (0·3 g.); the mother-liquors were diluted with water, and further crystallisation gave 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenazine (0·5 g.).

(iv) *Isomeride, m. p.* 147°, *with catalyst* B. The bulk of the product, collected as before,

melted at 120—124°, and proved to be a mixture of the two 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine isomerides. A more complete conversion into the 156°-isomeride was obtained on repassage.

(v) *Isomeride, m. p.* 109°, *with catalysts* A *and* B. No change occurred after three passages under the above conditions.

Nitroso-compounds of the Reduced Phenazines (I).—0·1 G. was dissolved in dilute sulphuric acid (5 c.c.), and sodium nitrite (0·1 g.) added; after a few minutes, excess of urea was added, and the product extracted with ether; this was dried, and removed under reduced pressure at room temperature, as warming caused decomposition. The product was crystallised from alcohol. 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydrophenazine, m. p. 156°, thus yielded a *dinitroso*-compound, m. p. 126° (Found: C, 58·55; H, 5·7. $C_{12}H_{14}O_2N_4$ requires C, 58·6; H, 5·7%); and 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine, m. p. 147°, a *dinitroso*-compound, m. p. 109° (Found: C, 58·3; H, 5·8%).

Dehydrogenation of the Octahydrophenazines with Palladium Charcoal.—Each of the three compounds (0·1 g.) was independently mixed with palladium charcoal (0·05 g.) in a small, loosely stoppered tube and heated in an oil-bath at 200° for ½ hour. A yellow sublimate of phenazine was obtained (about 0·06 g.), m. p. 171°, after crystallisation from light petroleum. Tetrahydrophenazine was similarly dehydrogenated.

Our thanks are due to Mr. O. Telfer for microanalyses, and one of us (H. McI.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

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56. *The Mechanism of the Conversion of Δ^{γ}-Butenol into Δ^{β}-Butenyl Bromide.*

By L. W. J. NEWMAN and H. N. RYDON.

LINSTEAD and RYDON (*J.*, 1934, 1995) found that Δ^{γ}-butenol (I; X = OH), on treatment with a hot mixture of sulphuric and hydrobromic acids, afforded a mixture of Δ^{β}-butenyl

(I.) $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2X$ $\qquad$ $CH_3{\cdot}CH{:}CH{\cdot}CH_2X$ (II.)

bromide (II; X = Br) and Δ^{γ}-butenyl bromide (I; X = Br), and pointed out that this apparent tautomeric change was unusual in that the propene system is separated from the only polar atom by a methylene group. Other work (Boorman, Linstead, and Rydon, J., 1933, 568; Linstead and Rydon, *ibid.*, p. 580) indicates that such activation through an intervening methylene group is improbable; for this reason it was decided to investigate the reaction more closely.

For the quantitative investigation it was necessary to develop methods for the analysis of mixtures of Δ^{β}- and Δ^{γ}-butenols and of the corresponding bromides. A suitable reaction for the two alcohols was their esterification by means of hydrobromic acid (*d* 1·48) at room temperature, Δ^{β}-butenol reacting readily, and Δ^{γ}-butenol not at all. For the analysis of mixtures of the bromides the reverse reaction was employed, Δ^{β}-butenyl bromide being hydrolysed, and the Δ^{γ}-isomeride unattacked, at room temperature in aqueous acetone.

The alcohols are unchanged after 100 hours' boiling. Prévost (*Ann. Chim.*, 1928, **10**, 147) has shown that Δ^{β}-butenyl acetate is hydrolysed by alkali without isomerisation; we have confirmed this and also shown that the same is true for Δ^{γ}-butenyl acetate. Moreover, the alcohols are recovered practically unchanged after being heated for 48 hours with 30% potassium hydroxide solution at 100°. It is thus evident that the isomeric change is not readily brought about by the alkaline reagents generally employed for effecting such reactions.

Since the isomerisation was first observed in the presence of acids, a number of acid catalysts were tried, but without success, the alcohols being recovered almost unchanged after boiling with acetic anhydride and with acetic acid, followed by the hydrolysis of the acetates produced. The slight changes observed are attributed either to the presence of

impurities, since the purification of small amounts of the alcohols was a matter of some difficulty, or to the operation of the mechanism advanced below; it is evident, however, that there is no question of the setting up of a reversible equilibrium, since the small apparent change is not increased by prolonged treatment. Attention was next directed to the bromides; once again the action of heat alone, of hot 50% sulphuric acid, and of hot hydrobromic acid (*d* 1·48) brought about no detectable migration of the double bond.

When, however, Δ^{γ}-butenol was distilled from a mixture of hydrobromic and sulphuric acids under the conditions used in the original observation (Linstead and Rydon, *loc. cit.*), the bromide formed was found to be a mixture containing 74% of the Δ^{β}-isomeride. Under the same conditions, Δ^{β}-butenol afforded no Δ^{γ}-butenyl bromide.

This suggested that a preliminary dehydration of Δ^{γ}-butenol to butadiene occurred, followed by 1 : 4-addition of hydrogen bromide :

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH \xrightarrow{-H_2O} CH_2{:}CH{\cdot}CH{:}CH_2 \xrightarrow{+HBr} CH_3{\cdot}CH{:}CH{\cdot}CH_2Br$$

Strong evidence in favour of this hypothesis was obtained in two ways. (1) When Δ^{γ}-butenol was treated with sulphuric acid under approximately the same conditions as those obtaining in the conversion into the bromide, butadiene was formed (identified as its tetrabromide). (2) Passage of butadiene through a hot mixture of sulphuric and hydrobromic acids of the same concentration as that used in the preparation of the bromide afforded a product, the lower-boiling portion of which (the monobromo-compound) was a mixture of 89% of Δ^{β}-butenyl bromide with 11% of the Δ^{γ}-isomeride. The higher proportion of the Δ^{γ}-butenyl bromide in the product from Δ^{γ}-butenol is probably due to a certain amount of direct esterification.

The simple analytical methods developed in this work were applied in a study of the isomerisation of α-methylallyl alcohol to Δ^{β}-butenol. Although the result was unsuccessful, it is desirable, in view of Young and Winstein's work (*J. Amer. Chem. Soc.*, 1935, **57**, 2013), to draw attention to some of the results so obtained. α-Methylallyl alcohol and the derived bromide were found to react, under the standard conditions, to the same extent as the corresponding Δ^{β}-butenyl compounds. Although not surprising, in view of the rapidity with which the equilibrium $CH_2{:}CH{\cdot}CHMeX \rightleftharpoons CH_3{\cdot}CH{:}CH{\cdot}CH_2X$ is set up (cf., *inter alia*, Baudrenghien, *Bull. Soc. chim. Belg.*, 1922, **31**, 160; Bouis, *Ann. Chim.*, 1928, **9**, 410; Young and Winstein, *loc. cit.*), this result shows that, whatever the proportion of α-methylallyl derivatives in our Δ^{β}-butenyl compounds, the whole would react on analysis as if it were the pure Δ^{β}-butenyl derivative; this possible variable factor is, therefore, without influence on our results.

Experimental.

Δ^{γ}-Butenol was prepared by the method of Linstead and Rydon (*loc. cit.*) and finally purified by repeated distillation over quicklime; the pure alcohol had b. p. 114°, $d_{4^\circ}^{20^\circ}$ 0·8531, $n_D^{20^\circ}$ 1·4109, $[R_L]_D$ 20·90 (calc., 21·70). It was characterised as its 3 : 5-*dinitrobenzoate*, m. p. 59° (Found : N, 10·7. $C_{11}H_{10}O_6N_2$ requires N, 10·5%); the *p*-nitrobenzoate and the phenylurethane are oils.

Δ^{γ}-Butenol was converted into the bromide by means of phosphorus tribromide and pyridine (Linstead and Rydon, *loc. cit.*); Δ^{γ}-butenyl bromide had b. p. 98—102°, $d_{4^\circ}^{20^\circ}$ 1·3280, $n_D^{20^\circ}$ 1·4627, $[R_L]_D$ 27·83 (calc., 27·97) (Found : Br, 58·8. Calc. : Br, 59·2%). When it was refluxed with silver 3 : 5-dinitrobenzoate in dry ether for 2 hours, Δ^{γ}-butenyl 3 : 5-dinitrobenzoate was produced, m. p. and mixed m. p. 59°.

Preparation of Δ^{β}-Butenol (Crotyl Alcohol).—The methods described in the literature give only poor yields; the following is an improvement of the procedure of Charon (*Ann. Chim. Phys.*, 1899, **17**, 215) : A suspension of 400 g. of crotonaldehyde in 4 l. of water was added to zinc–copper couple prepared from 400 g. of zinc foil, 635 c.c. of glacial acetic acid were added, and the mixture was kept at room temperature until the odour of crotonaldehyde was no longer perceptible (about 3 days). The liquid was filtered, made alkaline with sodium hydroxide, and distilled in steam. From the distillate, saturated with potassium carbonate, ether extracted a product, which was dried with potassium carbonate and fractionated. The fraction, b. p. 117—122°, on repeated distillation over quicklime, gave Δ^{β}-butenol (40—60 g.), b. p. 119°, $d_{4^\circ}^{20^\circ}$ 0·8496, $n_D^{20^\circ}$ 1·4222, $[R_L]_D$ 21·54 (calc., 21·70). The alcohol was characterised as its

p-*nitrobenzoate*, m. p. 44° (Found: N, 6·6. $C_{11}H_{11}O_4N$ requires N, 6·3%), 3 : 5-dinitrobenzoate, m. p. 51°, mixed m. p. with Δ^{γ}-butenyl 3 : 5-dinitrobenzoate, 47—48° (Found: N, 10·5. Calc. for $C_{11}H_{10}O_6N_2$: N, 10·5%), and *phenylurethane*, m. p. 65° (Found: N, 7·7. $C_{11}H_{13}O_2N$ requires N, 7·7%).

Δ^{β}-Butenyl Bromide.—A mixture of Δ^{β}-butenol (45 g.) and pyridine (14 g.) was added during 3 hours with mechanical stirring to phosphorus tribromide (67 g.) at 0°. The mixture was then distilled until frothing, accompanied by nauseous fumes, occurred. The distillate was washed with alkali and water, dried over calcium chloride, and redistilled. Yield, 42 g. (50%); b. p. 101—104°, $d_{4°}^{20°}$ 1·3280, $n_D^{20°}$ 1·4616, $[R_L]_D$ 27·96 (calc., 27·97) (Found: Br, 59·4. Calc.: Br, 59·2%). The 3 : 5-dinitrobenzoate prepared from it had m. p. and mixed m. p. 51°.

Analytical Methods.—(i) *Mixtures of Δ^{β}- and Δ^{γ}-butenol.* The mixture was weighed (0·5 g.) into a 100 c.c. measuring flask, treated with 2 c.c. of hydrobromic acid (*d* 1·48; previously standardised against *N*/20-sodium carbonate), and kept at room temperature for 2 hours. The mixture was then made up to 100 c.c. with water and 10 c.c. portions were titrated against *N*/20-sodium carbonate. The composition of the mixture was read off from a reference curve plotted from the following data, obtained with artificial mixtures and 8·83*N*-hydrobromic acid:

Δ^{β}-Butenol, %	0	22·7	45·2	59·0	100
Reaction, %	0	13·9	30·9	38·2	62·7

(ii) *Mixtures of Δ^{β}- and Δ^{γ}-butenyl bromide.* The mixture was weighed (0·5 g.) into a 100 c.c. measuring flask, dissolved in 50 c.c. of purified acetone, made up to 100 c.c. with water, and kept at room temperature for 24 hours; aliquot portions were then titrated with *N*/20-sodium carbonate, and the percentage hydrolysis calculated. The composition of the mixture was read off from a reference curve plotted from the following results, obtained with synthetic mixtures:

Δ^{β}-Butenyl bromide, %	0	16·0	43·0	85·0	100
Hydrolysis, %	0	9·8	29·3	62·7	70·4

Attempted Isomerisation of the Alcohols.—(i) *Action of heat.* (a) Δ^{β}-Butenol was boiled under reflux. Analysis showed the product to contain 100% of Δ^{β}-butenol after 24 hours, and 98% after 72 hours.

(b) Δ^{γ}-Butenol, treated similarly, was unchanged after 100 hours.

(ii) *Action of potassium hydroxide.* (a) 3 G. of Δ^{β}-butenol were heated at 100° in a sealed tube with 8 c.c. of 30% aqueous potassium hydroxide. The product contained 98·5% of Δ^{β}-butenol.

(b) An exactly similar experiment with Δ^{γ}-butenol gave a product containing 96% of Δ^{γ}-butenol.

(iii) *Action of acetic acid.* (a) A mixture of 5 g. of Δ^{β}-butenol and 10 g. of acetic acid was heated under reflux at 110—115° for 6 hours and poured into 80 c.c. of 10% sodium carbonate solution. The acetate was extracted with ether, dried, and distilled. The product, b. p. 120—128°, was hydrolysed with hot 30% aqueous sodium hydroxide and then distilled in steam. The alcohol, isolated from the distillate in the usual way, had b. p. 117—119° and contained 96% of Δ^{β}-butenol (3 : 5-dinitrobenzoate, m. p. 51°; mixed m. p. with authentic Δ^{β}-butenyl 3 : 5-dinitrobenzoate, 50—51°).

(b) A similar experiment with Δ^{γ}-butenol yielded a product, b. p. 112—114°, containing 93% of Δ^{γ}-butenol.

(iv) *Action of acetic anhydride.* (a) A similar experiment (6 hours' heating) with Δ^{β}-butenol, acetic anhydride being used in place of acetic acid, gave a product, b. p. 117—119°, consisting of pure Δ^{β}-butenol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 51°). A similar experiment in which the time of heating was 24 hours also gave pure Δ^{β}-butenol.

(b) A similar experiment (6 hours' heating) with Δ^{γ}-butenol yielded a product, b. p. 112—114°, containing 91% of Δ^{γ}-butenol (3 : 5-dinitrobenzoate, m. p. 59°; mixed m. p. with authentic Δ^{γ}-butenyl 3 : 5-dinitrobenzoate, 57°). A similar experiment in which the time of heating was 24 hours gave a product containing 94% of Δ^{γ}-butenol.

Attempted Isomerisation of the Bromides.—(i) *Action of heat.* Δ^{β}- and Δ^{γ}-Butenyl bromide were each heated for 24 hours in sealed tubes at 100°; the products were found on analysis to be the unchanged bromides.

(ii) *Action of sulphuric acid or hydrobromic acid.* Either bromide was heated at 100° in a sealed tube with an equal volume of 50% (by vol.) sulphuric acid or with one-quarter of its

volume of hydrobromic acid (*d* 1·48) for 24 hours. The product was shown by analysis to be unchanged bromide in every case.

Action of a Mixture of Hydrobromic and Sulphuric Acids on the Alcohols.—10 G. of the alcohol were added to a mixture of hydrobromic and sulphuric acids (prepared by reduction with sulphur dioxide of 14·3 g. of bromine and 18·5 g. of ice); to the hot stirred solution, 9 c.c. of concentrated sulphuric acid were added drop by drop, the distillate being collected until nothing further passed over. The product was washed with dilute sodium hydroxide solution and with water, dried, and distilled, the fraction, b. p. 97—106°, being collected. The product from Δ^{β}-butenol was found, on analysis, to consist of pure Δ^{β}-butenyl bromide. The product from Δ^{γ}-butenol was hydrolysed under the standard conditions to the extent of 55%; it was, therefore, a mixture of 74% of Δ^{β}-butenyl bromide with 26% of the Δ^{γ}-isomeride.

Butenyl Bromide from Butadiene.—Butadiene (generated from the tetrabromide) was passed into a hot mixture of hydrobromic and sulphuric acids of the composition used in the last experiment. The distillate was collected and worked up. The lower-boiling fraction, b. p. 98—105° (Found: Br, 58·9. Calc. for C_4H_7Br: Br, 59·2%), was hydrolysed to the extent of 65% under the standard conditions; it therefore contained 89% of Δ^{β}-butenyl bromide and 11% of the Δ^{γ}-compound. When it was refluxed for 2 hours in dry ether with silver 3 : 5-dinitrobenzoate, Δ^{β}-butenyl 3 : 5-dinitrobenzoate was obtained, m. p. and mixed m. p. 49—50°.

Butadiene from Δ^{γ}-Butenol.—10 G. of Δ^{γ}-butenol were added drop by drop to 25 c.c. of 50% (by vol.) sulphuric acid at 120°. The vapours were passed through a condenser to remove liquid products, and the uncondensed gas led into an ice-cooled mixture of bromine and water. The excess of bromine was destroyed with sulphur dioxide, and the solid twice crystallised from light petroleum, yielding butadiene tetrabromide, m. p. 116° (mixed m. p. 115—116° with an authentic specimen).

Experiments with α-Methylallyl Alcohol.—The alcohol was prepared from methylmagnesium iodide and acraldehyde (Delaby, *Bull. Soc. chim.*, 1923, **33**, 603; Bouis, *Ann. Chim.*, 1928, **9**, 402) and had b. p. 96—98°. On treatment with hydrobromic acid under the standard conditions (p. 263) the percentage reaction was 21·8 after 15 minutes and 58 after 1 hour (the corresponding figures for Δ^{β}-butenol were 29·4 and 60·2).

α-Methylallyl bromide was prepared from the alcohol by the phosphorus tribromide–pyridine method (cf. p. 263) and had b. p. 95—105°. Under the standard conditions it was hydrolysed to the extent of 69%, which is almost identical with the corresponding result for Δ^{β}-butenyl bromide.

An attempt to apply the bromometric method of Linstead (*J.*, 1927, 355) was unsuccessful, since the amount of addition was small and the rate of addition to α-methylallyl alcohol only slightly greater than to Δ^{β}-butenol. Methods based on the hydrogenation of the alcohols were also unsuccessful.

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Imperial College, London, S.W. 7. [*Received, December 6th,* 1935.]

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57. *The Formation of Organo-metalloidal Compounds by Micro-organisms. Part IV. Dimethyl-*n*-propylarsine and Methylethyl-*n*-propylarsine.*

By Frederick Challenger and Alan A. Rawlings.

Penicillium brevicaule (*Scopulariopsis brevicaulis*) *Saccardo* in bread cultures containing arsenious acid and its salts gives trimethylarsine (Challenger, Higginbottom, and Ellis, J., 1933, 95; Challenger and Higginbottom, *Biochem. J.*, 1935, **29**, 1757). With alkyl-arsonic and -arsinic acids, $R{\cdot}AsO_3H_2$ and $R_2AsO{\cdot}OH$,* mixed alkylmethylarsines, $AsRMe_2$ and AsR_2Me, are obtained (J., 1933, 97; 1935, 396). Sodium selenate and selenite give dimethyl selenide (Challenger and North, J., 1934, 68). The present communication describes two further instances of the methylating action of this mould as applied to methyl-*n*-propylarsinic and ethyl-*n*-propylarsinic acids (Wigren, *J. pr. Chem.*, 1930, **126**,

* These acids would now be named dialkylarsonic acids.—Ed.

223) whereby dimethyl-*n*-propylarsine (J., 1935, 396) and *methylethyl*-n-*propylarsine* are obtained.

The analyses, m. p.'s, and mixed m. p.'s obtained for the derivatives of methylethyl-*n*-propylarsine produced by the mould leave no doubt regarding its identity. Any possibility that the mould might have removed an ethyl or a propyl group from ethylpropylarsinic acid, giving rise to dimethyl-*n*-propylarsine (J., 1935, 397) or dimethylethylarsine (J., 1933, 99), is eliminated by a comparison of the m. p.'s of the derivatives of these two arsines and those of methylethyl-*n*-propylarsine.

In view of the ease with which these biological methylations occur, it is somewhat surprising that the mould appears incapable of producing phenyldimethylarsine from phenylarsonic acid in the form of its monopotassium salt (approximate concentration in the medium, 0·5%) either in bread or glucose–Czapek-Dox cultures. That this failure is not due to any inhibition of the methylation processes of the mould exerted by the aromatic compound would appear from the fact that, when a slightly impure phenylarsonic acid (containing arsenious acid) is added to bread cultures, trimethylarsine is evolved and readily detected as the dimercurichloride (J., 1933, 99). The question is under further investigation.

The methylating action exerted on arsonic and arsinic acids having now been established, it is not proposed to elaborate this reaction further as regards simple aliphatic compounds of this type containing only one arsenic atom, except in so far as is necessary to establish the mechanism of the reaction. In this connexion it was shown by one of us and Higginbottom (*Biochem. J.*, 1935, **29**, 1766) that with α-arsonopropionic acid * and bread cultures of the mould no dimethylethylarsine was produced and only the barest traces of trimethylarsine, which presumably arose from the presence of a trace of inorganic arsenic or from the hydrolysis to arsenic acid which the arsono-fatty acids undergo. Experiments with α-arsono-*n*-butyric acid (Backer and Mulder, *Proc. K. Akad. Wetensch. Amsterdam*, 1928, 31, 301) in bread cultures have now yielded very similar results. Neither dimethyl-*n*-propylarsine nor trimethylarsine could be detected by Biginelli's solution in two experiments each lasting 42 days. This additional evidence of the failure of the mould to decarboxylate derivatives containing the group $\vdots CH{\cdot}CO_2H$ (compare J., 1934, 69) weakens still further the theory that acetic acid is the biological methylating agent.

Experimental.

P. brevicaule Saccardo (*Baarn Strain A*) *and Methyl*-n-*propylarsinic Acid*.—Three 1 l. flasks, each containing 150 g. of bread and 20—30 c.c. of water, were sterilised, inoculated, and incubated for 4 days at 30°, and 25 c.c. of a sterile 1% solution of methyl-*n*-propylarsinic acid (kindly supplied by Dr. Nils Wigren, of Uppsala) added to each. Concentration, approx. 0·2%. The flasks were connected in series, and volatile products aspirated in a stream of sterile air into Biginelli's solution (mercuric chloride in hydrochloric acid; J., 1933, 96). After 21 days, 0·03 g. of a white precipitate, m. p. 196° (decomp.), had formed in the solution. This was recrystallised once from hot water containing a little mercuric chloride and then had m. p. 194°, decomp. 199°, alone or in admixture with synthetic dimethyl-*n*-propylarsine dimercurichloride (m. p. 194°, decomp. 199°; Challenger and Ellis, J., 1935, 398). In admixture with a further specimen (m. p. 195°, decomp. 200°) obtained by the same authors from *n*-propylarsonic acid and bread cultures of the mould, the m. p. was 194°, decomp. 198—199°. The quantity of dimercurichloride thus obtained was insufficient for analysis, but the m. p.'s given above and the analyses recorded (J., 1935, 397) for the dimercurichloride of dimethyl-*n*-propylarsine (of both synthetic and biological origin) clearly establish its identity.

The Biginelli's solution was then replaced by nitric acid (*d* 1·41), and aspiration continued for a further 22 days. The acid was then evaporated, and the last traces removed by repeated evaporation with water. Saturated aqueous sodium picrate then gave a yellow precipitate (0·06 g.), m. p. 140—141°. On recrystallisation from hot water this had m. p. 142—143° alone and 142·5—144° in admixture with synthetic dimethyl-*n*-propylhydroxyarsonium picrate (m. p. 143·5—144·5°; J., 1935, 397) (Found: C, 34·0; H, 4·4; N, 10·9. Calc. for $C_{11}H_{16}O_8N_3As$: C, 33·6; H, 4·1; N, 10·7%).

* There wrongly given (p. 1759) the formula of the β-compound.

P. brevicaule Saccardo *and Ethyl-*n*-propylarsinic Acid.—Methylethyl-*n*-propylarsine Dimercurichloride.* Four 1 l. flasks, each containing 150 g. of bread crumbs and 20—30 c.c. of water, were sterilised, inoculated as usual, and incubated for 4 days at 30° and for 1 day at room temperature. To each flask were added 25 c.c. of a sterile 1·2% aqueous solution of ethyl-*n*-propylarsinic acid. Concentration, 0·2%. A garlic odour was perceptible in the empty bottle (used as a trap and for observation) which was placed before the Biginelli's solution, after 3 days. A solid was deposited on the 5th day and increased very slowly; yield, 0·06 g. in 79 days. A second experiment yielded 0·05 g. in 73 days; and a third, 0·07 g. in 80 days. The deposits melted at 170°, decomposed at 186°, and after recrystallisation from hot water containing a little mercuric chloride melted at 171—172°, decomposed at 187°, and did not depress the m. p. of synthetic methylethyl-*n*-propylarsine dimercurichloride, m. p. 171—172°, decomp. 188° (Found: C, 9·8; H, 2·1; Cl, 20·0. Calc. for $C_6H_{15}Cl_4AsHg_2$: C, 10·2; H, 2·15; Cl, 20·1%).

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*Methylethyl-*n*-propylarsine dimercurichloride.* The arsine (1 c.c.) was added to an excess (80 c.c.) of Biginelli's solution. A white precipitate formed immediately and the mixture was left over-night and filtered. The solid, m. p. 168—170°, was recrystallised three times from hot water containing a little mercuric chloride, the recorded m. p.'s being 170—171°, 171—172°, 171—172°. In each case decomposition occurred at 188—189°. Addition of potassium hydroxide to a boiling aqueous solution gave a precipitate containing mercuric and mercurous oxides and mercury. Chlorine was determined in the filtrate (Found: C, 9·9; H, 2·1; Cl, 20·4, 20·0; Hg, 57·2, 57·2. Calc. for $C_6H_{15}Cl_4AsHg_2$: C, 10·2; H, 2·15; Cl, 20·1; Hg, 56·9%).

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The authors thank the Royal Society and Imperial Chemical Industries, Ltd., for grants.

THE UNIVERSITY, LEEDS. [*Received, December 18th,* 1935.]

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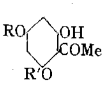
By KHUSSHAL C. GULATI and KRISHNASAMI VENKATARAMAN.

THE Friedel–Crafts reaction between phloroglucinol trimethyl ether and acetyl chloride, at a low temperature and in the absence of a solvent, leads to phloracetophenone trimethyl ether; when this is heated with aluminium chloride, the dimethyl ether is formed (Kostanecki and Tambor, *Ber.*, 1899, **32**, 2260). The reaction in benzene or chlorobenzene solution leads, however, to a phloracetophenone monomethyl ether having the properties of one of the two compounds obtained by Sonn and Bülow (*Ber.*, 1925, **58**, 1691) by a Hoesch reaction between phloroglucinol monomethyl ether and acetonitrile; we have confirmed the constitution (I; R = H, R′ = Me) assigned to it by Sonn and Bülow by preparing a *monobenzyl* ether (I; R = CH_2Ph, R′ = Me), since hydroxyl in the *o*-position to a keto-group cannot be benzylated (Gulati, Seth, and Venkataraman, J., 1934, 1765). The monobenzyl ether condenses smoothly with aldehydes to form chalkones (see also Shinoda and Sato, *J. Pharm. Soc. Japan*, 1928, **48**, 220).



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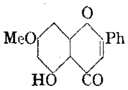

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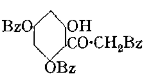

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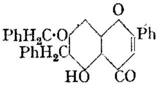

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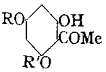

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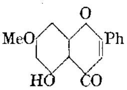

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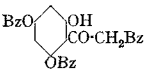

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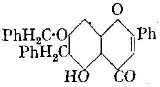

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Since the 5-hydroxyl in a flavone resembles the *o*-hydroxyl of a ketone in its resistance to facile methylation, it appeared probable that the ease with which an *o*-methoxy-ketone is demethylated would find a parallel in 5-methoxyflavones. This is so, the action of aluminium chloride on chrysin dimethyl ether (II) in nitrobenzene solution causing partial demethylation to tectochrysin (III). Heating (II) with solid aluminium chloride leads to a mixture of chrysin and tectochrysin, but (II) is the only product of the action of aluminium chloride on 2 : 4 : 6-trimethoxybenzoylacetophenone in nitrobenzene and subsequent treatment with alcoholic sulphuric acid. By the regulated action of hydriodic acid on 2 : 4 : 6-trimethoxybenzoylacetophenone, tectochrysin or chrysin or a mixture of both may be obtained, but apparently not (II).

Since Tasaki (*Acta Phytochim.*, 1925, **2**, 119) gives 115—117° as the m. p. of (II), whereas we find 143°, we have confirmed the constitution of our compound by its synthesis from *2-benzoyloxy-4 : 6-dimethoxyacetophenone* and sodamide (Mahal and Venkataraman, J., 1934, 1767; Bhalla, Mahal, and Venkataraman, J., 1935, 868). Although the action of benzoic anhydride on phloracetophenone leads ordinarily to chrysin (Robinson and Venkataraman, J., 1926, 2344), one experiment, after methylation of the product, gave, in addition to (II), its *3-benzoyl* derivative; treatment of the latter with aluminium chloride gave tectochrysin. The possibility of 3-acylation during the Robinson reaction has already been indicated (Anderson, *Canadian J. Research*, 1932, **7**, 285; Chadha and Venkataraman, J., 1933, 1074). Another by-product of the condensation of phloracetophenone and benzoic anhydride has been formulated as (IV) (compare Baker, J., 1933, 1381).

The benzylation of chrysin under various conditions gave only 5-hydroxy-7-benzyloxy-6-benzylflavone (V) with the usual properties of a 5-hydroxyflavone.

Experimental.

2 : 4 : 6-*Trimethoxyacetophenone*.—In place of ferric chloride (Kostanecki and Tambor, *loc. cit.*), the condensation between phloroglucinol trimethyl ether (25 g.) and acetyl chloride (26 g.), at − 5° to − 10°, is more conveniently carried out with aluminium chloride (13 g.), added during 3 hours. After 3 hours, ice is added, and the product (19 g.), m. p. 110°, isolated in the usual manner.

2 : 4-*Dihydroxy*-6-*methoxyacetophenone* (I; R = H, R′ = Me).—When a mixture of 2 : 4 : 6-trimethoxyacetophenone (1 g.), aluminium chloride (1 g.), and chlorobenzene (10 c.c.) was refluxed for 1 hour, the solvent removed by steam-distillation, and the residue cooled, cream-coloured needles (from alcohol) were obtained (0·3 g.), m. p. 203° (Sonn and Bülow, *loc. cit.*, give m. p. 205—207°) (Found : C, 59·2; H, 5·5. Calc. for $C_9H_{10}O_4$: C, 59·3; H, 5·5%). The alcoholic solution gave a deep red colour with ferric chloride.

2-*Hydroxy*-4-*benzyloxy*-6-*methoxyacetophenone* (I; R = CH_2Ph, R′ = Me).—Benzylation of the preceding ketone as in the case of resacetophenone (Gulati, Seth, and Venkataraman, *loc. cit.*) and crystallisation from aqueous alcohol gave colourless needles, m. p. 72° (Found : C, 70·5; H, 5·9. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

Chrysin Dimethyl Ether.—(a) The reaction between chrysin (0·2 g.) and methyl sulphate (1 c.c.) in acetone (10 c.c.) and 20% caustic soda solution (2·5 c.c.), first in the cold and then on the water-bath, gave chrysin dimethyl ether (0·1 g.), which formed colourless needles, m. p. 143°, from dilute alcohol (Found : C, 72·1; H, 4·9. Calc. for $C_{17}H_{14}O_4$: C, 72·3; H, 4·9%).

(b) 2-*Benzoyloxy*-4 : 6-*dimethoxyacetophenone* was prepared by heating 2-hydroxy-4 : 6-dimethoxyacetophenone (1 g.) with benzoyl chloride (1 g.) and pyridine (2 g.) for 15 minutes. Treatment with hydrochloric acid and ether extraction gave colourless needles, m. p. 91° (from alcohol) (Found : C, 68·1; H, 5·3. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). The benzoate (1 g.) was shaken with sodamide (1 g.) and ether (15 c.c.) and the deep chocolate-brown solid was collected, washed with ether, and treated with ice and acetic acid. The diketone separated as an oil and was converted into the chromone by boiling with 20% alcoholic sulphuric acid (20 c.c.) for 2 hours. Crystallisation from alcohol gave colourless needles (0·4 g.), m. p. 143°, identical with (II).

(c) To a solution of aluminium chloride (1·4 g.) in nitrobenzene (10 c.c.), 2 : 4 : 6-trimethoxybenzoylacetophenone (0·7 g.) was added. After 12 hours, the mixture was treated with ice, and the nitrobenzene removed by steam-distillation. The cooled residue was partly crystalline and contained 2-hydroxy-4 : 6-dimethoxydibenzoylmethane as indicated by the ferric chloride coloration. It was collected, washed with dilute hydrochloric acid, boiled for 2 hours with 20% alcoholic sulphuric acid (20 c.c.), and poured into water. One crystallisation of the product from alcohol gave (II), m. p. 143° (0·5 g.).

Tectochrysin (III).—(a) A solution of aluminium chloride (0·2 g.) and (II) (0·2 g.) in nitrobenzene (5 c.c.) was heated on the water-bath for 1 hour, cooled, and treated with dilute hydrochloric acid and the product was collected after steam-distillation of the solvent. Crystallisation from alcohol gave colourless needles (0·12 g.), m. p. 165° (Found : C, 71·5; H, 4·7. Calc. for $C_{16}H_{12}O_4$: C, 71·6; H, 4·5%). The ferric chloride coloration was deep red. After (II) (0·5 g.) had been heated with a like amount of aluminium chloride at 115° for 30 minutes, treatment with ice–hydrochloric acid and fractional crystallisation from aqueous alcohol gave tectochrysin (0·08 g.) and chrysin (0·15 g.), m. p. 275°. (b) 2 : 4 : 6-Trimethoxybenzoylaceto-

phenone (0·5 g.) was heated with hydriodic acid (*d* 1·7; 5 c.c.) and acetic anhydride (5 c.c.) for 5 minutes and poured into sodium bisulphite solution. Crystallisation of the product from alcohol gave (III) (0·2 g.), m. p. 165°. When the heating was prolonged to 20 minutes, a minute amount of (III) and 0·2 g. of chrysin were obtained.

3-*Benzoylchrysin Dimethyl Ether.*—The crude product (2 g.), in one experiment, of the Robinson reaction with phloracetophenone and benzoic anhydride, obtained by precipitation with carbon dioxide, was treated with acetone (20 c.c.), 10% caustic soda solution (35 c.c.), and methyl sulphate (25 g.) with mechanical stirring during 2 hours. Dilution with water and two crystallisations from acetone gave yellow needles (0·3 g.), m. p. 212° (Found : C, 74·8; H, 4·8. $C_{24}H_{18}O_5$ requires C, 74·6; H, 4·7%). Evaporation of the mother-liquors and recrystallisation of the residue from alcohol gave chrysin dimethyl ether (0·6 g.), m. p. 143°.

In a second experiment, phloracetophenone (5 g.) gave chrysin (2·2 g.), which was twice recrystallised from alcohol. When the mother-liquors were concentrated to small bulk and cooled, cream-coloured needles (0·5 g.), m. p. 157°, of 2-*hydroxy*-4 : 6-*dibenzoyloxy*-ω-*benzoylacetophenone* (IV) separated (Found : C, 72·2; H, 4·4. $C_{29}H_{20}O_7$ requires C, 72·5; H, 4·2%). When the substance was hydrolysed with alkali, the odour of acetophenone became perceptible. The alcoholic solution gave a deep red colour with ferric chloride. Dissolution in sulphuric acid and treatment with ice led to a mixture, which, however, after hydrolysis with 10% alcoholic caustic potash, precipitation with carbon dioxide, and crystallisation from alcohol, gave chrysin, m. p. 275°.

5-*Hydroxy*-7-*benzyloxy*-6-*benzylflavone* (V).—(a) Benzylation of chrysin in the known manner (Gulati, Seth, and Venkataraman, *loc. cit.*) with benzyl chloride, acetone, and potassium carbonate, and crystallisation of the product from acetone, gave yellow needles, m. p. 205° (Found : C, 80·3; H, 5·4. $C_{29}H_{22}O_4$ requires C, 80·2; H, 5·1%). (b) To a solution of caustic potash (0·25 g.) in alcohol, chrysin (0·5 g.) and benzyl bromide (0·4 g.) were added. After being shaken for a few minutes, the mixture was warmed on the water-bath for ½ hour. The orange precipitate was collected and washed with dilute hydrochloric acid, and the product crystallised from acetone, giving pale yellow needles (0·3 g.), m. p 205°, identical with the benzyl ether obtained in (a).

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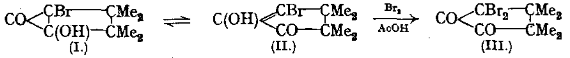
59. 1 : 2 : 3-*Triketotetramethyl*cyclo*pentane : A Blue Triketone.*

By CHARLES W. SHOPPEE.

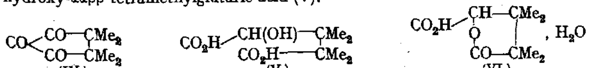
INVESTIGATIONS of cyclic derivatives of phorone (Francis and Willson, J., 1913, 103, 2238; Ingold and Shoppee, J., 1928, 365, 1868; Shoppee, J., 1928, 1662, 2360) had shown that the orange-coloured compound obtained from the tautomeric bromohydroxy-compounds (I, II) by bromination in an ionising solvent has the structure (III). Its most characteristic reaction is the facile elimination of one bromine atom (cf. Ingold and Shoppee, *loc. cit.*, p. 380) with regeneration of the bromohydroxy-compound (I, II). By treating it with



(I.) (II.) (III.)

an excess of hot alcoholic sodium acetate, however, Francis and Willson obtained a colourless bromine-free compound, m. p. 100°, which they regarded as a diacetate, and which afforded a substance, m. p. 68°, also obtained directly from (III), by the action of aqueous potassium hydroxide.

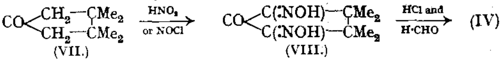
It is now shown that the supposed diacetate is the *hydrate* of 1 : 2 : 3-*triketotetramethyl*cyclo*pentane* (IV), and that the substance, m. p. 68°, is the *lactonic acid monohydrate* (VI) of γ-hydroxy-ααββ-tetramethylglutaric acid (V).



(IV.) (V.) (VI.)

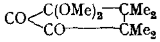
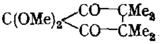
The hydrate of the triketone (IV) was obtained, but not isolated, by the author in 1928 from 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone (VII) by treatment with nitrous acid or

nitrosyl chloride, and subsequent hydrolysis of the dioximino-compound (VIII) with hydrochloric acid and formaldehyde, and was characterised by formation of a trioxime.

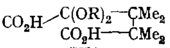
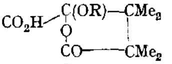
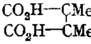


(VII.) (VIII.)

When the dibromo-diketone is refluxed with sodium or potassium acetate in methyl alcohol, the hydrate of the triketone (IV) or a *molecular compound* of the triketone hydrate and the anhydrous triketone (see below) is obtained. If, however, silver acetate is substituted for sodium or potassium acetate, the product is the crimson-red *dimethoxy*-1 : 2-*diketone* (IX). Further, if the dibromo-diketone is refluxed with absolute methyl-alcoholic potassium hydroxide, the colourless *dimethoxy*-1 : 3-*diketone* (X) is rapidly produced.

(IX.)   (X.)

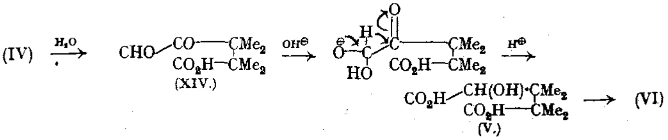
In accordance with the structure of a 1 : 2-diketone suggested by its magnificent crimson-red colour, the compound (IX) readily affords a 2 : 4-*dinitrophenylosazone* (but not a quinoxaline). It is oxidised by hydrogen peroxide in acetone at 0° to give γγ-dimethoxy-ααββ-tetramethylglutaric acid (XI; R = Me), which during isolation loses methyl alcohol to yield the *lactonic acid* (XII; R = Me) of γ-hydroxy-γ-methoxy-ααββ-tetramethylglutaric acid. Oxidation at 15° gives the same products together with tetramethylsuccinic acid (XIII).

(XI.) (XII.) (XIII.)

The dimethoxy-diketone (IX) is stable to warm aqueous potassium hydroxide, but readily hydrolysed by hydrochloric acid in aqueous acetone to the triketone hydrate (IV), which partly recombines with the methyl alcohol produced to give the dimethoxy-1 : 3-diketone (X). The last-named substance yields a 2 : 4-*dinitrophenylhydrazone*, and gives the triketone hydrate by hydrolysis with hydrochloric–acetic acid.

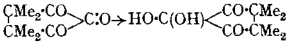
The triketone hydrate, now isolated in a state of purity, is a colourless crystalline substance, m. p. 95°. It reduces Fehling's solution instantaneously in the cold, and rapidly produces silver from cold ammoniacal silver nitrate. When warmed with aqueous solutions of α-amino-acids, it affords deep blue colours analogous to those given by triketohydrindene (Ruhemann, J., 1910, **97**, 2030). It is readily soluble in, and decomposes, sodium carbonate solution (compare the similar acidity of the hydrates of triketopentane and triketohexane; Sachs and Wolff, *Ber.*, 1903, **36**, 3222). The triketone hydrate gives a *hydrate monosemicarbazone* instantaneously, an anhydrous 2 : 4-*dinitrophenylhydrazone*, and a 2 : 4-*dinitrophenylosazone* (which may be alternatively a 1 : 3-*bis*-2′ : 4′-*dinitrophenylhydrazone*); with *o*-phenylenediamine it affords a *quinoxaline*, and by complete oximation the trioxime referred to above. By oxidation with hydrogen peroxide in acetone at 0°, it gives principally tetramethylsuccinic acid, together with traces of the precursor of this, namely, γ-keto-ααββ-tetramethylglutaric acid, isolated as the lactonic acid (XII; R = H) which results by additive ring-closure of the foregoing ketonic acid (Rothstein and Shoppee, J., 1927, 531; Ingold and Shoppee, *loc. cit.*, p. 380). The triketone hydrate is converted almost quantitatively by cold 50% aqueous potassium hydroxide into the lactonic acid hydrate (VI) of γ-hydroxy-ααββ-tetramethylglutaric acid (V). This product undoubtedly arises by the following series of changes (cf. Shoppee, J., 1928, 1662):

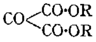


The reaction is precisely analogous to the transformation of triketohydrindene into *o*-carboxymandelic acid (Ruhemann, J., 1910, **97**, 1448, 2026) and explains the isolation of (VI), as recorded by Francis and Willson (*loc. cit.*), by the action of potassium hydroxide on their supposed diacetate or on the dibromo-diketone (III).

The most striking characteristic of the triketone hydrate (IV) is its behaviour on dehydration; this occurs partially and reversibly (a) when it is melted, the colourless melt rapidly becoming bright green, (b) when its colourless solutions in anhydrous non-hydroxylic media (di-*n*-propyl ether, ligroin, acetone, carbon tetrachloride, benzene, ethylene dibromide, benzonitrile, camphor) are heated, the depth of the blue-green colour developed increasing with temperature up to *ca.* 120—130°. Partial dehydration also occurs on vacuum distillation; complete dehydration, although difficult to attain, is brought about by repeated distillation with phosphoric oxide in a vacuum. The anhydrous triketone obtained by distillation is a solid of intense bright blue-green colour; it crystallises from carbon tetrachloride–ligroin in deep blue prisms, the highest recorded m. p. being 164°. The triketone appears to possess considerable affinity for water, and gradually becomes converted, even in a vacuum in a desiccator, into a colourless molecular compound of triketone and triketone hydrate (probably XV). The triketone naturally exhibits all the reactions of (IV) and (XV).

The blue colour of the triketone must be ascribed to the contiguous association of the three carbonyl groups. The closest analogue yet described, 1 : 2 : 3-triketo*cyclo*pentane, has been obtained only as the colourless hydrate (Reichstein and Oppenhauer, *Helv. Chim. Acta*, 1934, **17**, 390), but all the anhydrous αβγ-tricarbonyl compounds recorded in the literature combine with water to yield colourless hydrates, and, with a single exception, all vary in colour from orange to red. The sole exception is the ester of ketomalonic acid (XVI; R = Me or Et), which is a green liquid giving a colourless crystalline hydrate with great ease (Curtiss and Spencer, *J. Amer. Chem. Soc.*, 1909, **31**, 1053; Curtiss and Stracham, *ibid.*, 1911, **33**, 396).

(XV.) 

 (XVI.)

The absorption spectra of the blue triketone, and of the red diketone (IX) for comparison, show that the blue colour is due to an absorption band with a maximum at 685 mμ (carbon tetrachloride) and the red colour of the diketone is similarly due to an unsymmetrical band at 510 mμ (alcohol). The ultra-violet absorption spectra of the two compounds are distinctly different (see table).

	Blue Triketone (IV).			Red Diketone (IX).
Solvent.	Alcohol.	Chloroform (B.P.).*	Carbon tetrachloride.	Alcohol.
Colour of solution.	None	After ½ minute, none	Blue	Red
Absorption maxima in mμ.†	346, 311, (298)	345, 309, (295)	685, 367, *ca.* 313, (301)	510, (482), 322, 309, 294, 283 group of narrow bands
ε (at respective wave-lengths).	61, 54, 36	40, 53, —	8·4, 39, 47, —	58, —, 36, 55, 58, 64
Active substance present.	Triketone hydrate	Triketone hydrate	Triketone	Diketone

* Contains alcohol, hence the conversion into the hydrate.
† Inflexions in brackets.
Molar extinction coefficient, ε, = density/(molar concentration × thickness in cm.).

The blue colour of the anhydrous triketone, at first sight somewhat unusual, is only an example of the general rule that conjugation of chromophoric groups tends to displace colour in the direction yellow ⟶ red ⟶ blue; in other words, that conjugation tends to displace the absorption bands towards longer wave-lengths. The fact that this triketone is blue whereas simple tricarbonyl compounds are orange or red may be due to a possible auxochromic action of the two CMe_2 group on the three carbonyl groups; alternatively,

the cyclic structure may contribute to the observed effect. The green colour of the ketomalonic esters cannot be dependent upon such accessory factors.

The lactonic acid (VI) exists as the monohydrate, which is not dehydrated at 50° in a vacuum over phosphoric oxide and behaves as a monobasic acid on titration. It was first obtained by the author by reduction of the lactonic acid (XII, R = H) with sodium amalgam, during a repetition of Francis and Willson's original experiments; the product had the m. p. and properties described by Francis and Willson and was not analysed. Since, however, the analyses recorded by Francis and Willson indicate the anhydrous lactonic acid, the original specimen, prepared in 1928, a new specimen obtained by the same method, and the specimen furnished by the foregoing pinacolic change have been analysed : in all three cases identical figures are obtained which correspond to those required for the monohydrate.

EXPERIMENTAL.

1 : 1-Dibromo-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanedione (III) was obtained as described by Francis and Willson (*loc. cit.*; compare Ingold and Shoppee, *loc. cit.*, p. 408). Owing to the extreme ease with which the compound reverts to the parent bromo-hydroxy-ketone, crystallisation is difficult except on the smallest scale. By use of dry di-*n*-propyl ether, the product being in solution for the least time possible, the dibromo-diketone (80 g.) was obtained in large orange rhomboids, m. p. 182°.

1 : 2 : 3-*Triketotetramethyl*cyclo*pentane Hydrate*.—The dibromo-diketone and an equal weight of fused sodium acetate were refluxed with absolute methyl alcohol for 6 hours; the yellow solution was filtered from precipitated sodium bromide, and methyl alcohol largely removed by evaporation. The product, which contained acetic acid, was dissolved in ether, washed with water, dried (sodium sulphate), and recovered as a yellow oil which crystallised after 1—2 weeks. The solid, after draining on porcelain and crystallisation from ether–ligroin (b. p. 40—60°), furnished 1 : 2 : 3-*triketotetramethyl*cyclo*pentane hydrate* in colourless leaflets, m. p. 95° to a colourless liquid which rapidly turned bright green [Found : C, 58·1; H, 7·6; *M* (cryoscopic in glacial acetic acid), 183, 193. $C_9H_{14}O_4$ requires C, 58·1; H, 7·6%; *M*, 186]. Use of fused potassium acetate and/or ethyl alcohol gave the same result.

The triketone hydrate reacted instantaneously with alcoholic semicarbazide acetate to give the *hydrate monosemicarbazone*, which formed colourless plates, m. p. 153° (decomp.), from dilute methyl alcohol (Found : C, 49·3; H, 7·3; N, 17·6. $C_{10}H_{17}O_4N_3$ requires C, 49·4; H, 7·05; N, 17·3%). With 2 : 4-dinitrophenylhydrazine sulphate it furnished the anhydrous 2 : 4-*dinitrophenylhydrazone*, which crystallised from ethyl acetate or ethyl alcohol in clusters of orange prisms, m. p. 219—220° (Found : C, 51·5; H, 4·5; N, 16·2. $C_{15}H_{16}O_6N_4$ requires C, 51·7; H, 4·6; N, 16·6%); the action of excess of the reagent during a longer period afforded the 2 : 4-*dinitrophenylosazone* (?1 : 3-*bis*-2′ : 4′-*dinitrophenylhydrazone*), which separated from much ethyl alcohol as a crystalline brick-red powder, m. p. 268—270° (decomp.) (Found : N, 20·6. $C_{21}H_{20}O_9N_8$ requires N, 21·2%). A *quinoxaline*, readily obtained, crystallised from dilute alcohol in fine yellow prisms, m. p. 108° (Found : C, 74·5; H, 6·7; N, 11·7. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7; N, 11·7%). Complete oximation gave the trioxime, m. p. and mixed m. p. 169°.

The triketone hydrate is stable to potassium permanganate in cold acetone, but is oxidised on warming. It is slightly soluble in cold water, but dissolves in cold aqueous sodium carbonate, and is partly extracted from ethereal solution with this reagent. The observed depressions of m. p. in camphor lead to anomalous molecular weights (Found : *M*, 545, 554, 535, 554). The hydrate stains the skin violet-brown.

The Molecular Compound (XV).—In a repetition of the foregoing preparation of the triketone hydrate, the yellow oily product was kept in a vacuum over potassium hydroxide to remove acetic acid, since, owing to the acid nature of the triketone hydrate, washing with sodium carbonate solution cannot be employed. The oil gradually solidified, and the solid crystallised from ether–ligroin (b. p. 40—60°) or from ligroin (b. p. 100—120°) in colourless prisms, m. p. 119—120° to a green liquid. The substance was identified as a *molecular compound* of 1 : 2 : 3-triketotetramethyl*cyclo*pentane (1 mol.) and its hydrate (1 mol.) [Found : C, 61·0; H, 7·4; OMe, 0; *M* (cryoscopic in glacial acetic acid), 340, 343. $C_{18}H_{26}O_7$ requires C, 61·0; H, 7·4%; *M*, 354]. It gave blue colours with hot α-amino-acid solutions, stained the skin, and furnished the hydrate semicarbazone, m. p. 153° (decomp.) (Found : C, 49·6; H, 7·1; N, 17·2%), the osazone, m. p. 268—270°, and the quinoxaline, m. p. 108° (Found : N, 11·6%), described

above; in each case, a mixed m. p. exhibited no depression. The compound gave blue-green solutions in hot non-hydroxylic solvents, and furnished anomalous molecular weights by the Rast method (Found : *M*, 497, 475).

Oxidation of the Triketone Hydrate.—Use of hydrogen peroxide in acetone at 0° in the presence of solid sodium bicarbonate gave principally tetramethylsuccinic acid, m. p. 193° (gas evolution), mixed m. p. 193°, after crystallisation from ethyl acetate; the ethyl acetate mother-liquors contained a small quantity of a more soluble acid, m. p. 135—138°, which was not identified with certainty, but was probably the lactone of γγ-dihydroxy-ααββ-tetramethylglutaric acid, m. p. 140°.

Transformation of the Triketone Hydrate into the Lactonic Acid Hydrate (VI).—When the triketone hydrate (0·5 g.) was treated with 50% aqueous potassium hydroxide (2 c.c.), solution occurred with evolution of heat and the transient appearance of a white crystalline solid; no sequence of colour changes such as those described by Ruhemann (J., 1910, 97, 1448) for triketohydrindene hydrate was observed. After ½ hour, the solution was acidified with ice-cold 2*N*-sulphuric acid and extracted with ether, and the extract dried (sodium sulphate) and evaporated. A solid acid (0·49 g.) was obtained, which after crystallisation from ethyl acetate–ligroin (b. p. 60—80°) had m. p. 68° and was identified as the *hydrate* of the lactonic acid of γ-hydroxy-ααββ-tetramethylglutaric acid [Found : C, 53·0; H, 8·0; *M*(Rast), 269, 281; *M* (by titration), 205. $C_9H_{14}O_4,H_2O$ requires C, 52·9; H, 7·9%; *M*, 204]. No depression of the m. p. was observed by admixture with a specimen, m. p. 68°, freshly prepared by Francis and Willson's method (*loc. cit.*) (Found : C, 53·1; H, 7·85%), or with the original specimen, m. p. 68°, prepared by Ingold and Shoppee in 1928 (*loc. cit.*) (Found : C, 52·9; H, 7·9%).

1 : 2 : 3-*Triketotetramethyl*cyclo*pentane* (IV).—When the pure triketone hydrate was heated in a vacuum (10 mm.; bath at *ca.* 140°), a blue crystalline solid passed over, which consisted largely of the anhydrous *triketone* (Found : C, 62·3; H, 7·4. $C_9H_{12}O_3$ requires C, 64·3; H, 7·2%). These microanalytical figures indicate the possible presence of 29% of triketone hydrate in the product; the pure triketone hydrate was therefore intimately mixed with phosphoric oxide, and maintained at 140°/760 mm. for ½ hour; then the pressure was reduced to 10 mm., and the blue triketone passed over and was immediately sealed up for microanalysis (Found : C, 62·4; H, 7·3%; in a repetition : C, 62·5; H, 7·25%, corresponding to 73% and 74% dehydration respectively). A specimen, prepared by a two-stage repetition of the distillation with phosphoric oxide in a one-piece all-glass apparatus and crystallised from dry carbon tetrachloride, was obtained in bright blue prisms, m. p. 164° (Found : C, 62·8; H, 7·3%, corresponding to 80% dehydration). (An alternative possibility is that the low carbon values are due to incomplete combustion; cf. Ingold and Shoppee, *loc. cit.*, p. 385.)

1 : 1-*Dimethoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione* (IX).—The dibromo-diketone (10 g.) silver acetate (20 g.), and absolute methyl alcohol were refluxed for 1 hour. Silver bromide and the excess of silver acetate were removed by filtration, and methyl alcohol by evaporation in a vacuum. The product (*A*) was dissolved in ether, washed with 2*N*-sodium carbonate and with water, dried (sodium sulphate), and recovered; after solidification, two crystallisations from ligroin (b. p. 40—60°) gave 1 : 1-*dimethoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione* (4 g.) in large rose-red cubes, m. p. 68° [Found : C, 61·6; H, 8·5; OMe, 28·6; *M* (Rast), 236, 239. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·45; OMe, 29·0%; *M*, 214]. The ketone is slightly volatile in methyl alcohol, but not in ether, and can be distilled in small quantities in a vacuum. With *o*-phenylenediamine in methyl alcohol, the red colour disappeared, but a crystalline quinoxaline could not be obtained. The 2 : 4-*dinitrophenylosazone* formed orange needles, m. p. 266° (decomp.), from much ethyl acetate or from xylene (Found : C, 48·1; H, 4·1; N, 20·5. $C_{23}H_{26}O_{10}N_8$ requires C, 48·1; H, 4·5; N, 19·5%). Small quantities of the triketone are also formed in the reaction, since the product (*A*) stained the skin violet.

On one occasion the reaction after prolongation for 18 hours yielded, not the dimethoxy-diketone, but exclusively the triketone hydrate. The product, a yellow oil, gave the triketone 2 : 4-dinitrophenylhydrazone (m. p. 218—220°; mixed m. p. 219—220°. Found : C, 51·6; H, 4·8; OMe, 0%), and crystallised on keeping; recrystallised from ether–ligroin (b. p. 40—60°), it separated in colourless leaflets of the triketone hydrate, m. p. 95°, mixed m. p. 95° (Found : C, 58·1; H, 7·7; OMe, 0%). This occurrence is believed to be connected with the specimen of silver acetate used, which may have contained sufficient occluded acid to cause hydrolysis of the dimethoxy-diketone, since it was not encountered in many subsequent repetitions in which various specimens of silver acetate and reflux-times up to 72 hours were employed.

Oxidation with hydrogen peroxide. To the dimethoxy-diketone (1 g.) in acetone at 0°, perhydrol (1 c.c.) was added drop by drop during stirring in the presence of sodium bicarbonate

(1 g.) and a trace of 2*N*-sodium hydroxide. The red colour of the solution slowly faded, and the colourless oil of peppermint-like odour remaining after removal of acetone by evaporation became crystalline over-night. After draining on porcelain, the product was twice crystallised from ligroin (b. p. 40—60°), the *lactone* of *γ-hydroxy-γ-methoxy-ααββ-tetramethylglutaric acid* being obtained as a colourless crystalline powder, m. p. 58°, soluble in sodium bicarbonate solution [Found: C, 56·0; H, 7·45; OMe, 14·9; *M* (Rast), 288, 295. $C_{10}H_{16}O_5$ requires C, 55·6; H, 7·45; OMe, 14·4%; *M*, 216]. Repetition at 15° gave a product, which was worked up into neutral and acidic fractions; the latter gave traces of the above lactonic acid, but consisted mainly of tetramethylsuccinic acid, m. p. 193° (gas evolution) after crystallisation from ethyl acetate–ligroin (Found: C, 55·2; H, 8·1. Calc. for $C_8H_{14}O_4$: C, 55·2; H, 8·1%). The neutral fraction was too small for examination (Found: C, 60·1; H, 9·3; OMe, 27·2%).

Hydrolysis. The dimethoxy-diketone (10 g.), dissolved in acetone (50 c.c.), was heated with concentrated hydrochloric acid (5 c.c.) under reflux. The red colour of the solution gave place to yellow in a few minutes and the liquid was evaporated (4-bulb column). The residual oil was taken up in ether, washed with 2*N*-sodium carbonate, dried (sodium sulphate), and recovered as a yellow oil, which by rapid distillation gave a bright blue distillate, b. p. *ca.* 120°/10 mm. On cooling, blue crystals of the anhydrous triketone separated, which after filtration and washing with ligroin had m. p. 150—153° (Found: C, 62·8, 62·4; H, 7·1, 7·4%). When the filtrate was evaporated and cooled below 0°, large, almost colourless rhombs (2 g.) were deposited: these were identified as 2 : 2-dimethoxytetramethyl*cyclo*pentane-1 : 3-dione (see below), m. p. 62°, mixed m. p. 62°, after two crystallisations from ligroin (b. p. 40—60°). The sodium carbonate washings were acidified with hydrochloric acid, and repeatedly extracted with ether; the extract, after drying (sodium sulphate) and evaporation, gave practically pure triketone hydrate (1 g.), m. p. (crude) 92° (Found: C, 58·2; H, 7·5%).

1 : 1-Diethoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanedione, obtained by refluxing the dibromo-diketone with silver acetate in absolute alcohol, formed a rose-red oil containing more than 30% of ethoxyl (Calc., 37·2%).

2 : 2-*Dimethoxytetramethyl*cyclo*pentane*-1 : 3-*dione* (X).—The dibromo-diketone (3 g.) reacted violently with a warm solution of potassium hydroxide (1·25 g.) in absolute methyl alcohol (25 c.c.) with separation of potassium bromide and formation of a rose-pink solution; after 1 hour's heating on the steam-bath, methyl alcohol was removed by evaporation and the product was dissolved in ether, washed with water, dried (sodium sulphate), and recovered. The resulting oil, which from its red colour contained some of the 1 : 1-dimethoxy-isomeride (IX), and also contained some of the triketone hydrate, since it stained the skin, crystallised readily when cooled below 0°. Draining and washing with a little cold ligroin on porous porcelain removed the red colour, and after two crystallisations from ligroin (b. p. 40—60°) 2 : 2-*dimethoxytetramethyl*cyclo*pentane*-1 : 3-*dione* was obtained in very long, colourless prisms, m. p. 62° [Found: C, 61·6; H, 8·5; OMe, 28·8; *M* (Rast), 200, 201. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·45; OMe, 29·0%; *M*, 214]. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate–alcohol in brick-red leaflets, m. p. 184° (Found: C, 52·0; H, 5·4; N, 14·5. $C_{17}H_{22}O_7N_4$ requires C, 51·8; H, 5·6; N, 14·2%). Hydrolysis with 50% acetic acid containing a little hydrochloric acid in an open vessel to facilitate the removal of methyl alcohol and/or methyl acetate furnished the triketone hydrate.

Acknowledgment is made of the preparation of phorone in quantity by British Drug Houses, Ltd., and of a grant from the Chemical Society for its purchase. The author wishes to thank Prof. I. M. Heilbron, D.S.O., F.R.S., and Mr. A. E. Gillam for their kindness in connexion with the measurements of absorption spectra.

The University of Leeds. [*Received, December 19th, 1935.*]

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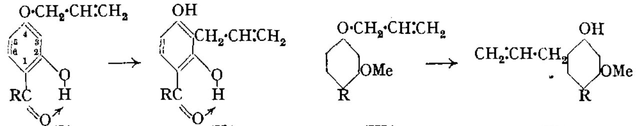
60. *Studies in Chelation. Part III. The Stabilisation of Kekulé Forms in* o-*Hydroxy-carbonyl Compounds.*

By Wilson Baker and (Miss) O. M. Lothian.

It was shown in Part II (Baker and Lothian, J., 1935, 628) that the thermal rearrangement of 4-*O*-allylresacetophenone gave 3-allylresacetophenone, and that the rearrangement of 2-*O*-methyl-4-*O*-allylresacetophenone gave the differently oriented 2-*O*-methyl-5-allylres-

acetophenone. This behaviour was anticipated on the view that chelation between the hydroxyl and the acetyl group in *o*-hydroxyacetophenones depends upon the mutual unsaturation of the carbon atoms bearing these groups (see Part I; Baker, J., 1934, 1684) and therefore leads to stabilisation of one of the Kekulé forms, and in the rearrangement of 4-*O*-allylresacetophenone to the exclusive formation of 3-allylresacetophenone. In 2-*O*-methyl-4-*O*-allylresacetophenone, chelation is prevented by methylation, no stabilisation of Kekulé forms occurs, and migration of the allyl group leads to the symmetrical type of product usually given by resorcinol derivatives.

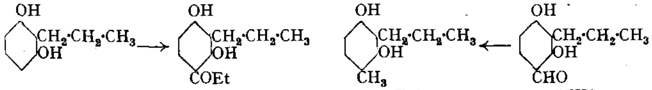
The same effect has now been found to occur in *o*-hydroxy-propiophenones and in *o*-hydroxy-aldehydes. 4-O-*Allylrespropiophenone* (I; R = Et) underwent molecular rearrangement on heating to give an 85% yield of 3-*allylrespropiophenone* (II; R = Et) as the only isolable compound. 2-O-*Methyl*-4-O-*allylrespropiophenone* (III; R = COEt) similarly gave an 80% yield of 2-O-*methyl*-5-*allylrespropiophenone* (IV; R = COEt), and in this case also no other product could be isolated.



(I.) (II.) (III.) (IV.)

Of β-resorcylaldehyde derivatives, 4-O-*allyl*-β-*resorcylaldehyde* (I; R = H) underwent thermal rearrangement to give a 50% yield of 3-*allyl*-β-*resorcylaldehyde* (II; R = H) as the only isolable compound, and 2-O-*methyl*-4-O-*allyl*-β-*resorcylaldehyde* (III; R = CHO) gave a 59% yield of 2-O-*methyl*-5-*allyl*-β-*resorcylaldehyde* (IV; R = CHO). The poorer yields of the aldehyde derivatives are due to the reactive nature of the aldehyde group.

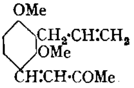
The derivatives of respropiophenone were prepared and oriented in the following manner. Allylation of respropiophenone in acetone solution with allyl bromide and potassium carbonate gave the 4-*O*-allyl ether (I; R = Et), the position of the allyl group being proved by the formation of a chelate *copper* derivative soluble in chloroform. The position of the allyl group in 3-allylrespropiophenone was proved by catalytic reduction to 3-n-*propylrespropiophenone* (VI), a compound which was independently synthesised from 2-*n*-propylresorcinol (V) (Part II, *loc. cit.*) and propionitrile under the conditions of the Hoesch synthesis. Methylation of (I; R = Et) in acetone solution with methyl sulphate gave the methyl ether (III; R = COEt). The position of the allyl group in (IV; R = COEt) was established by conversion into the methyl ether, 5-*allylrespropiophenone dimethyl ether*, m. p. 67°, which was not identical with the dimethyl ether of (II; R = Et), 3-*allylrespropiophenone dimethyl ether*, b. p. 180°/18 mm.

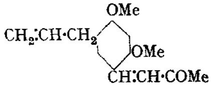


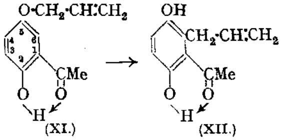
(V.) (VI.) (VII.) (VIII.)

β-Resorcylaldehyde was converted by allylation into the 4-*O*-allyl ether (I; R = H), and thence by methylation into (III; R = CHO). The last compound was also produced by allylation of the known 2-*O*-methyl ether of β-resorcylaldehyde, a fact which proves the position of the allyl group in (I; R = H). The orientation of (II; R = H) was established by catalytic reduction in presence of palladium chloride, both the allyl group and the aldehyde group being completely reduced with formation of 4-*methyl*-2-n-*propylresorcinol* (VII), a compound which was independently synthesised from 2-*n*-propylresorcinol by conversion into 3-n-*propyl*-β-*resorcylaldehyde* (VIII), and subsequent catalytic reduction.

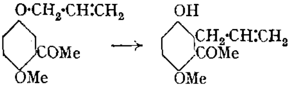
Methylation of (II; R = H) and (IV; R = CHO) with methyl sulphate and alkali in acetone solution led to the two isomeric compounds 2 : *4-dimethoxy-3-allylstyryl methyl ketone* (IX), m. p. 45°, and 2 : *4-dimethoxy-5-allylstyryl methyl ketone* (X), m. p. 76°, the non-identity of which proves the position of the allyl group in (IV; R = CHO). The complete methylation of (II; R = H) in the absence of acetone presented difficulties, and in presence of acetone the methylated styryl methyl ketone was obtained, the same condensation taking place in the case of (IV; R = CHO); solid isomeric products were thus obtained for direct comparison.

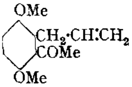

(IX.)

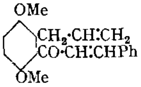

(X.)


(XI.) (XII.)

An attempt was made to detect the possible fixation of a Kekulé form in 2 : 5-dihydroxyacetophenone (quinacetophenone) in a similar manner. Molecular rearrangement of 2-*hydroxy-5-allyloxyacetophenone* (XI) yielded 2 : *5-dihydroxy-6-allylacetophenone* (XII) in 74% yield in accordance with expectations. From 2-*methoxy-5-allyloxyacetophenone* (XIII), the methyl ether of (XI) in which chelation is impossible, was, however, obtained in 94% yield the methyl ether of (XII), namely, *5-hydroxy-2-methoxy-6-allylacetophenone* (XIV). The "natural" position of substitution in non-chelate derivatives of 2 : 5-dihydroxyacetophenone is hence identical with the position of substitution to be expected *on the grounds of a fixed Kekulé structure as in* (XI), unlike the case of the resorcinol derivatives previously studied. These experiments, therefore, do not afford evidence of a stable Kekulé form in 2 : 5-dihydroxyacetophenone, but are entirely in harmony with the view that such a stable form exists.


(XIII.) (XIV.)


(XV.)


(XVI.)

Allylation of quinacetophenone gave the 5-*O*-allyl ether (XI), the compound being shown to be an *o*-hydroxyacetophenone by the formation of a chelate copper derivative. Methylation of (XI) yielded (XIII). The similar orientation of (XII) and (XIV) was shown by the fact that on methylation they both gave 2 : *5-dimethoxy-6-allylacetophenone* (XV) (liquid), characterised in each case by the formation of the benzylidene derivative, 2 : *5-dimethoxy-6-allylphenyl styryl ketone* (XVI). The position occupied by the nuclear allyl group in these compounds followed from the fact that under no conditions could 2 : 5-dimethoxy-6-allylacetophenone (XV) be converted into a semicarbazone, the suppression of carbonyl reactivity being obviously due to steric influences. Such influences could be operative only if the allyl group occupied position 6. The correctness of this view was established by the fact that the isomeric 2 : 4-dimethoxy-3-allylacetophenone yielded a *semicarbazone* with extreme ease, as do all the known dimethoxyacetophenones.

In attempts to apply the present methods to derivatives of 4-ethylresorcinol, β-resorcylic acid, 4-nitroresorcinol, and nitroquinol, the following compounds were prepared : *4-ethylresorcinol diacetate*; *4-ethylresorcinol diallyl ether*; *4-O-allyl-β-resorcylic acid*; *ethyl* 4-O-*allyl-β-resorcylate*; *4-nitroresorcinol* 1-O-*allyl ether*; *4-nitro-6* (or 2)-*allylresorcinol*; *nitroquinol diallyl ether*; *2-nitroquinol* 4-O-*allyl ether*. In these cases the rearrangement of the allyl ethers did not take place sufficiently smoothly to warrant a continuation of the experiments.

EXPERIMENTAL.

4-O-*Allylrespropiophenone* (I; R = Et).—A mixture of respropiophenone (73 g.; 1 mol.; dried in a vacuum over sulphuric acid), anhydrous potassium carbonate (80 g.), and allyl bromide (54 g.; 1 mol.) in acetone (160 c.c.) was refluxed and stirred on the water-bath for 7 hours. After acidification the product was extracted with ether, and precipitated therefrom as the very sparingly soluble sodium salt by shaking with 10% aqueous sodium hydroxide (700 c.c.). The salt was collected on a sintered glass funnel, washed with ether, and decomposed by the addition of hydrochloric acid. The liberated 4-O-*allylrespropiophenone* was taken up in ether and isolated as a colourless oil, b. p. 174°/14 mm. (Found: C, 69·6; H, 6·7. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·9%). It gave an intense reddish-brown coloration with alcoholic ferric chloride.

The *copper* derivative was prepared by shaking a solution of the compound (2 g.) in alcohol (20 c.c.) with saturated aqueous copper acetate (40 c.c.) containing 2 drops of dilute aqueous ammonia. The green product, which solidified completely on rubbing, was collected, washed with water and then alcohol, and to the filtered solution in warm chloroform (10 c.c.) was added alcohol (10 c.c.). The copper derivative separated in blue-green prismatic needles, m. p. 158° (darkening and partial decomposition) (Found: C, 59·9; H, 5·8; Cu, 12·2. $C_{24}H_{26}O_6Cu,EtOH$ requires C, 60·0; H, 6·2; Cu, 12·2%. The presence of alcohol was proved qualitatively by heating).

3-*Allylrespropiophenone* (II; R = Et).—4-*O*-Allylrespropiophenone (3·6 g.) was heated in an oil-bath at 205° for 2 hours. The product crystallised completely on cooling to an almost white mass, m. p. 114—118°. A quantity (3·4 g.) of this crude product, crystallised from benzene–light petroleum (b. p. 40—60°) (40 c.c. of each), yielded colourless material (2·4 g.), m. p. 123—124°. By working up the mother-liquor, a further quantity (0·6 g.) of slightly crude product, m. p. 118—120°, was obtained. The results show that the total yield is not less than 85%. Pure 3-*allylrespropiophenone* separated from benzene–ligroin in small plates, m. p. 124° (Found: C, 69·7; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·9%). Its alcoholic or dilute alcoholic solution gave an intense purplish-brown colour with ferric chloride.

3-n-*Propylrespropiophenone* (VI).—(A) A mixture of 2-*n*-propylresorcinol (1 g.) (Baker and Lothian, *loc. cit.*), propionitrile (2 c.c.), dry ether (20 c.c.), and anhydrous zinc chloride (1 g.) was saturated with hydrogen chloride at 0°. After 24 hours, addition of water threw down a very sparingly soluble zinc-containing derivative of the ketimine, which was not hydrolysed by heating with dilute hydrochloric acid containing zinc chloride. After separation from the acid solution it was, however, rapidly hydrolysed by heating with water, and the *ketone* separated as an oil which became solid on cooling (1·1 g.). It separated from very dilute alcohol in colourless nacreous plates, m. p. 109—110° (Found: C, 68·9; H, 8·0. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). (B) 3-Allylrespropiophenone (1 g.) was reduced in alcohol (15 c.c.) with hydrogen in presence of palladium chloride (0·15 g.). Absorption of hydrogen was complete in 1 hour, and evaporation of the filtered solution left a solid, which was crystallised first from light petroleum (b. p. 60—80°) and then from dilute alcohol and obtained in nacreous plates, m. p. 109—110° either alone or when mixed with that prepared by method (A).

3-*Allylrespropiophenone Dimethyl Ether*.—3-Allylrespropiophenone (2·5 g.) in acetone (50 c.c.) was shaken with the alternate addition of methyl sulphate (25 c.c.) and excess of 20% potassium hydroxide solution, the mixture being finally heated on the water-bath for ½ hour. An ethereal extract of the product was washed with 20% potassium hydroxide solution, then with water, dried, and distilled, leaving an oil, b. p. 180°/18 mm., $n_D^{15°}$ 1·540 (Found: C, 71·8; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

2-O-*Methyl*-4-O-*allylrespropiophenone* (III; R = COEt).—4-*O*-Allylrespropiophenone (36 g.) was treated in acetone (200 c.c.) with methyl sulphate (100 c.c.) and 20% aqueous potassium hydroxide in the usual manner, the mixture being allowed to boil. After heating on the steam-bath for ½ hour with excess of alkali, the product was diluted, and extracted with ether, and the extracts were shaken with dilute sodium hydroxide solution, dried, and distilled, leaving an oil (38 g.) which solidified on cooling. Its solution in light petroleum (b. p. 40—60°), when cooled to 0°, deposited fibrous needles, m. p. 31° (Found: C, 70·9; H, 7·4. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

2-O-*Methyl*-5-*allylrespropiophenone* (IV; R = COEt).—2-*O*-Methyl-4-*O*-allylrespropiophenone was heated for 2 hours at 200°. The pasty product (1·65 g.) was shaken with dilute sodium hydroxide solution and ether; the ethereal layer yielded unchanged material (0·70 g.), m. p. 30—31°; the alkaline layer was acidified, and the crystalline 2-O-*methyl*-5-*allylrespropio*-

phenone collected and dried (yield, 0·95 g.; m. p. about 115°). After crystallisation from a little benzene and then from dilute alcohol (charcoal) it was obtained as fine prismatic needles, m. p. 132—133° (Found: C, 70·9; H, 7·3. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). The yield of pure product (0·77 g.) was 80% of the theoretical, calculated on the weight of (III; R = COEt) which had undergone rearrangement.

5-Allylresropiophenone Dimethyl Ether.—2-*O*-Methyl-5-allylresropiophenone in 10% sodium hydroxide solution was shaken with excess of methyl sulphate at about 60°. The alkali-insoluble product solidified on cooling, and was collected, washed, and dried; it crystallised from light petroleum (b. p. 40—60°) in curved prismatic needles, m. p. 67° (Found: C, 71·8; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

4-O-*Allyl-β-resorcylaldehyde* (I; R = H).—A mixture of β-resorcylaldehyde (22 g.; 1 mol.), anhydrous potassium carbonate (40 g.), and allyl bromide (19·2 g.; 1 mol.) was refluxed and stirred on the water-bath for 7 hours. After removal of most of the acetone by distillation the residue was acidified with dilute hydrochloric acid and extracted with ether. The ethereal layer was now shaken with 8% sodium hydroxide solution, and β-resorcylaldehyde and its monoallyl ether liberated from the alkaline solution by addition of acid and separated by distillation in steam, in which only the latter was volatile. The steam-distillate yielded 4-O-*allyl-β-resorcylaldehyde* (9 g.) as a colourless oil, b. p. 149—150°/13 mm. (Found: C, 67·1; H, 5·4. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). Its alcoholic solution gave an intense reddish-brown coloration with ferric chloride.

3-*Allyl-β-resorcylaldehyde* (II; R = H).—4-*O*-Allyl-β-resorcylaldehyde (5 g.) was heated in an oil-bath at 190—200° for 1 hour, the maximum temperature of the melt reaching 202°. The resulting dark red, sticky solid was decolourised by boiling with charcoal in alcoholic solution for 3 hours, and the recovered product recrystallised from carbon tetrachloride (yield, 2·5 g.). It separated in lustrous needles, m. p. 129—130° (Found: C, 67·3; H, 5·7. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%).

2-O-*Methyl*-4-O-*allyl-β-resorcylaldehyde* (III; R = CHO).—(A) 4-*O*-Allyl-β-resorcylaldehyde (6 g.) in acetone (150 c.c.) was methylated by the alternate addition of methyl sulphate (55 c.c.) and an excess of 20% aqueous potassium hydroxide in small quantities, the mixture being allowed to boil. After ½ hour the solution was extracted with ether, the extract shaken with 20% potassium hydroxide solution, aud distilled, leaving an oil which slowly solidified. The product separated from light petroleum (b. p. 40—60°) in colourless rhombic prisms, m. p. 45° (Found: C, 68·8; H, 6·4. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

(B) A mixture of 2-*O*-methyl-β-resorcylaldehyde (2·5 g.) (Gattermann and Berckelmann, *Ber.*, 1898, **31**, 1767), acetone (150 c.c.), potassium carbonate (15 g.), and allyl bromide (5 g.) was stirred under reflux on the water-bath for 6 hours. After removal of the acetone by distillation and addition of dilute aqueous sodium hydroxide, the solution yielded to ether a solid (3·1 g.), which, after crystallisation as before, formed prisms, m. p. 44—45°, not depressed by the specimen prepared by method (A).

2-*Methoxy*-4-*allyloxystyryl methyl ketone* was produced on one occasion in place of compound (III; R = CHO) in experiment (A) (above). It formed pale yellow crystals, m. p. 39—40°, from light petroleum (Found: C, 72·4; H, 7·0. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·8%). When mixed with (III; R = CHO), it melted at 25—30°.

2-O-*Methyl-5-allyl-β-resorcylaldehyde* (IV; R = CHO).—2-*O*-Methyl-4-*O*-allyl-β-resorcylaldehyde (1·83 g.) was heated at 220° for 1 hour, the maximum temperature reached by the melt being 203°. The dark semi-solid product was dissolved in ether, and the solution shaken with aqueous sodium hydroxide. The ether yielded unchanged initial material (0·67 g.), and the alkaline solution after acidification yielded to ether a rather dark solid (1·04 g.). This was crystallised from light petroleum (500 c.c.; b. p. 80—100°) and a faintly yellow product (total yield, 0·69 g.), m. p. 135—140°, was obtained [yield of this product, calculated on the amount of (III; R = CHO) which underwent change, 59%]. The pure *substance* separated from hot water in rhombic prisms, m. p. 145—146° (Found: C, 68·6; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

2 : 4-*Dimethoxy-5-allylstyryl Methyl Ketone* (X).—2-*O*-Methyl-5-allyl-β-resorcylaldehyde (0·4 g.) in acetone (40 c.c.) was methylated at the boiling point in the usual way with methyl sulphate (10 c.c.) and excess of 20% aqueous potassium hydroxide during 1 hour. After removal of the acetone by distillation the product was extracted with ether, and the extract shaken with alkali, dried, and distilled, leaving a crystalline solid (0·47 g.). It separated from light petroleum (b. p. 60—80°) at 0° in small yellow crystals, m. p. 76—77° (Found: C, 73·2; H, 7·5. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%).

2 : *4-Dimethoxy-3-allylstyryl methyl ketone* (IX), prepared by methylation of 3-allyl-β-resorcylaldehyde in acetone as described in the previous case, separated from light petroleum (b. p. 40—60°) in small, very faintly yellow prisms, m. p. 45° (Found: C, 73·3; H, 7·2. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%).

4-Methyl-2-n-propylresorcinol (VII).—(A) 3-Allyl-β-resorcylaldehyde (1·5 g.) in alcohol (20 c.c.) was reduced at room temperature with hydrogen in presence of palladium chloride (0·13 g.). During 4 hours hydrogen corresponding to 3 molecules (500 c.c.) was absorbed, the first molecule (probably owing to the reduction of the allyl group) more rapidly than the other two. The filtered solution left an oil which solidified on scratching; it separated from light petroleum (b. p. 80—100°) in faintly pink needles, m. p. 96—97° (Found: C, 71·9; H, 8·4. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%). The substance sublimed in colourless feathery needles on the water-bath, and its solution in dilute alcohol gave no coloration with ferric chloride. (B) 3-*n*-Propyl-β-resorcylaldehyde (VIII) (below) was catalytically reduced under the conditions described in experiment (A), two molecules of hydrogen being absorbed. The product, twice crystallised from light petroleum, formed needles, m. p. 96—97°, either alone or when mixed with the specimen prepared by method (A), and the two substances were identical in all properties.

3-n-Propyl-β-resorcylaldehyde (VIII).—2-*n*-Propylresorcinol (0·4 g.) (Baker and Lothian, *loc. cit.*; compare Nesmejanow and Sarewitsch, *Ber.*, 1935, 68, 1478) in anhydrous ether (10 c.c.) containing liquid hydrogen cyanide (2 c.c.) was slowly saturated at 0° with dry hydrogen chloride. After 12 hours, an equal volume of dry ether was added, and the ether was decanted from the solid aldimine hydrochloride, which was then hydrolysed by heating with water (15 c.c.) for 20 minutes. The solid *aldehyde* separated on cooling and was recrystallised from boiling water (20 c.c.), forming colourless fibrous needles, m. p. 92—93° (Found: C, 66·3; H, 6·6. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). Its alcoholic solution gave a deep brown coloration with ferric chloride.

2-Hydroxy-5-allyloxyacetophenone (XI).—A mixture of 2 : 5-dihydroxyacetophenone (19 g.; 1 mol.), allyl bromide (16 g.; 1 mol.), and anhydrous potassium carbonate (25 g.) in acetone (50 c.c.) was refluxed and stirred on the water-bath for 9 hours. After dilution with water, the mixture was shaken with a large volume of ether, and the ethereal extract shaken twice with water and then with 20% aqueous sodium hydroxide (200 c.c.). The sodium salt of 2-hydroxy-5-allyloxyacetophenone at once separated as yellow crystalline plates, which were collected, washed with cold 20% sodium hydroxide solution, then with ether, and decomposed with dilute hydrochloric acid. The oily product rapidly solidified, and was collected, washed, and dried (17·5 g.); it separated from light petroleum (b. p. 40—60°) in large, thick, almost rectangular, pale yellow prisms, m. p. 59—60° (Found: C, 69·0; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·2%). It dissolved in aqueous sodium hydroxide with a yellow colour, and gave an intense indigo-blue coloration with alcoholic ferric chloride. When warmed with copper acetate solution as in the preparation of the copper derivative of (I; R = Et) and subsequently shaken with chloroform, it gave a green solution of a copper derivative. The derivative was readily soluble in benzene and chloroform, giving green solutions, but it could not easily be separated from the parent substance (XI).

2 : *5-Dihydroxy-6-allylacetophenone* (XII).—2-Hydroxy-5-allyloxyacetophenone (4 g.) was placed in an oil-bath at 180°, and the temperature raised during 35 minutes to 230°. After about 15 minutes, the slightly exothermic reaction caused the temperature of the melt to rise 4° higher than that of the oil-bath. The product solidified on cooling, and was collected (3·91 g.), crushed, and treated twice with boiling light petroleum (20 c.c.; b. p. 40—60°), the insoluble residue refluxed with carbon tetrachloride (150 c.c.), and the resulting solution filtered. It slowly deposited almost colourless plates, m. p. 105—106° (2·88 g.; 74% yield). Recrystallisation from a little benzene gave elongated rhombic plates, m. p. 107·5° (Found: C, 68·9; H, 6·2. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·2%). With alcoholic ferric chloride it gave a green coloration, fading rapidly to yellow, and with aqueous ferric chloride a transient blue.

2 : *5-Dimethoxy-6-allylacetophenone* (XV).—(A) 2 : 5-Dihydroxy-6-allylacetophenone was treated in acetone solution with much methyl sulphate and excess of 20% aqueous potassium hydroxide, finally on the water-bath for ½ hour. The methylated product was extracted with ether, and was isolated as a colourless oil, b. p. 164—165°/14 mm., $n_D^{13°}$ 1·534 (Found: C, 70·9; H, 7·4. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). (B) Methylation of 5-hydroxy-2-methoxy-6-allylacetophenone (below) in a similar manner gave a product, b. p. 164°/14 mm., $n_D^{13°}$ 1·535 (Found: C, 70·9; H, 7·2%). Neither specimen would yield a semicarbazone when treated with semicarbazide hydrochloride and sodium acetate in dilute alcohol under a wide variety

of conditions (compare formation of semicarbazone of 3-allylresacetophenone dimethyl ether, below).

2 : 5-Dimethoxy-6-allylphenyl Styryl Ketone.—Specimens (A) and (B) of 2 : 5-dimethoxy-6-allylacetophenone (above) were separately treated in alcoholic solution with benzaldehyde (1 equiv.) and a drop of 10% aqueous sodium hydroxide and left over-night. The diluted solutions yielded to ether yellow oils, which solidified and then crystallised (separately) from light petroleum (b. p. 60—80°) in pale yellow, stout, rectangular prisms, m. p. and mixed m. p. 75° (Found : C, 78·1; H, 6·5. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·4%).

2-Methoxy-5-allyloxyacetophenone (XIII).—2-Hydroxy-5-allyloxyacetophenone was methylated in acetone solution by the alternate addition of methyl sulphate and excess of 20% aqueous potassium hydroxide, with final heating on the water-bath for ½ hour. The methylated product was extracted with ether from the diluted liquid, and obtained as a colourless oil, b. p. 166°/13 mm., $n_D^{11°}$ 1·548 (Found : C, 69·8; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

5-Hydroxy-2-methoxy-6-allylacetophenone (XIV).—2-Methoxy-5-allyloxyacetophenone (2 g.) was placed in an oil-bath at 220°, the temperature of which was raised to 230° during 20 minutes. The maximum excess temperature of the melt over that of the bath was 1·5°. The solid product was dissolved in dilute aqueous sodium hydroxide, and, after the solution had been shaken with ether to remove the unchanged allyl ether, was reprecipitated by the addition of hydrochloric acid at 0°, collected, washed, and dried (1·57 g.). Crystallisation from carbon tetrachloride gave colourless rhombic prisms (1·40 g.), m. p. 104° (Found in material dried in a vacuum at 100° : C, 69·6; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). By working up the mother-liquors, a total of 1·48 g. of pure *5-hydroxy-2-methoxy-4-allylacetophenone* was obtained, equivalent to 94% of the theoretical yield from the alkali-soluble product of the rearrangement.

The *semicarbazone* of 3-allylresacetophenone dimethyl ether, prepared from 3-allylresacetophenone dimethyl ether (Baker and Lothian, *loc. cit.*) in the usual manner, separated from benzene in prismatic needles, m. p. 159—160° (Found : N, 15·0. $C_{14}H_{19}O_3N_3$ requires N, 15·2%).

4-Ethylresorcinol Diacetate.—4-Ethylresorcinol was boiled with an excess of acetic anhydride for 2 hours, the mixture shaken with water and extracted with ether, and the extracts shaken with aqueous sodium bicarbonate in excess, dried, and distilled, giving a colourless liquid, b. p. 162°/14 mm. (Found : C, 64·8; H, 6·4. $C_{12}H_{14}O_4$ requires C, 64·8; H, 6·3%). This compound is merely mentioned by Rosenmund, Buchwald, and Deligiannis (*Arch. Pharm.*, 1933, **271**, 344).

4-Ethylresorcinol diallyl ether, produced as the non-phenolic product when 4-ethylresorcinol was allylated in acetone solution with allyl bromide and potassium carbonate under the usual conditions, was a colourless oil, b. p. 146°/10 mm. (Found : C, 77·1; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·2%).

Ethyl 4-O-Allyl-β-resorcylate.—Ethyl β-resorcylate (36·4 g.), allyl bromide (25 g.), acetone (100 c.c.), and potassium carbonate were stirred and boiled under reflux for 8 hours. After dilution with water, the solution yielded to ether a low-melting solid (42 g.), which separated from alcohol (120 c.c.) in prismatic needles (20 g.), m. p. 42° (Found : C, 65·0; H, 6·2. $C_{12}H_{14}O_4$ requires C, 64·8; H, 6·3%). The alcoholic solution gave an intense purplish-red colour with ferric chloride.

4-O-Allyl-β-resorcylic acid, prepared by hydrolysis of the preceding ester with 10% sodium hydroxide solution, separated from 50% alcohol in prismatic needles, m. p. 155—156° (Found : C, 61·5; H, 5·3. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·1%). The ferric chloride reaction is similar to that given by the ester.

4-Nitroresorcinol.—The potassium salt of 4-nitrosoresorcinol was prepared, according to the directions of Henrich (*Ber.*, 1902, **35**, 4192), from resorcinol, alcoholic potassium hydroxide, and amyl nitrite. We were unable to convert the substance into 4-nitroresorcinol by oxidation with hydrogen peroxide under the conditions described by Borsche and Berkhout (*Annalen*, 1903, **330**, 106) and could only obtain traces of the desired product by the method of Gilbert, Laxton, and Prideaux (*J.*, 1927, 2299). The following method gives poor, but reproducible yields. A solution of the freshly prepared potassium salt of 4-nitrosoresorcinol (10 g.) in a mixture of 6% hydrogen peroxide (30 c.c.) and perhydrol (10 c.c.) was cautiously warmed until signs of reaction became apparent, and then placed in a vessel of cold water. A violent reaction occurred, which was allowed to continue for 5 minutes with occasional warming; the solution was cooled, acidified with 2*N*-sulphuric acid (10 c.c.), and extracted five times with chloroform (total volume 500 c.c.; 4-nitrosoresorcinol is insoluble in chloroform); the extracts were dried over sodium sulphate and distilled, leaving a bright yellow solid (0·5 g.). This separated from

hot water in needles of the hemi-hydrate; after dehydration at 70° it had m. p. 115°. The yield is not correspondingly increased by working with larger quantities.

4-*Nitroresorcinol* 1-O-*Allyl Ether*.—Anhydrous 4-nitroresorcinol (10 g.) in acetone (50 c.c.) was heated and stirred under reflux for 12 hours with allyl bromide (10 g.) and potassium carbonate (20 g.). After removal of most of the acetone and acidification with dilute hydrochloric acid, the products were extracted with ether, the extracts shaken with 15% sodium hydroxide solution, and the very sparingly soluble sodium salt of 4-nitroresorcinol 1-*O*-allyl ether collected on a sintered glass funnel and washed with a little sodium hydroxide solution and then with more ether. The sodium salt yielded the free *compound* as a pale yellow oil, b. p. 157—158°/10 mm. (Found: C, 55·9; H, 4·8. $C_9H_9O_4N$ requires C, 55·4; H, 4·6%).

4-*Nitro*-6 (or 2)-*allylresorcinol*.—4-Nitroresorcinol 1-*O*-allyl ether (2·5 g.) was heated at 185° for 50 minutes, and the product shaken with 10% sodium hydroxide solution. The insoluble sodium salt was collected, washed with ether, and decomposed by the addition of acid, yielding unchanged 4-nitroresorcinol 1-*O*-allyl ether (1·24 g.). The alkaline filtrate yielded to ether a solid (0·43 g.), m. p. 67—77°, which after two crystallisations from light petroleum (b. p. 40—60°) formed yellow prisms (0·32 g.; 26% yield on rearranged product), m. p. 85·5° (Found: C, 55·6; H, 4·8. $C_9H_9O_4N$ requires C, 55·4; H, 4·6%).

Nitroquinol Diallyl Ether.—This compound appears to be the sole product of the allylation of nitroquinol in acetone solution, although monoallylation may be effected in alcoholic solution (succeeding preparation). Nitroquinol (20 g.) in acetone (100 c.c.) was stirred under reflux for 6 hours with allyl bromide (15 g.; 1 mol.) and potassium carbonate (30 g.). Most of the acetone was removed by distillation, and the diluted solution was extracted with ether. Pure, unchanged nitroquinol was removed from the extract by shaking with alkali, and after evaporation of the ether the remaining oil solidified at 0°. The product separated from light petroleum (b. p. 40—60°) at 0° in light yellow needles, m. p. 22° (Found: C, 61·2; H, 5·6. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·4%).

2-*Nitroquinol* 4-O-*Allyl Ether*.—Nitroquinol [8 g.; conveniently prepared by demethylation of its dimethyl ether by boiling with 10 times its weight of a mixture of equal volumes of glacial acetic acid and hydrobromic acid (*d* 1·5) for 12 hours, and extracting the carefully neutralised solution with ether] in alcohol (50 c.c.) was refluxed for 6 hours with allyl bromide (6·2 g.; 1 mol.) and an alcoholic solution of sodium ethoxide (from 1·18 g. of sodium; 1 mol.). The diluted solution was made strongly alkaline, extracted with ether, then acidified, and subjected to steam distillation. The 2-*nitroquinol* 4-O-*allyl ether* (1 g.) collected from the distillate crystallised from light petroleum (b. p. 40—60°) in masses of fine, bright yellow needles, m. p. 48° (Found: C, 55·8; H, 4·5. $C_9H_9O_4N$ requires C, 55·4; H, 4·6%).

The authors' thanks are due to the Chemical Society for a grant, and to Mr. G. N. Carruthers for preparing 2-nitroquinol 4-*O*-allyl ether.

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61. 15-*Phenylpentadecoic Acid and* 22-*Phenylbehenic Acid.*

By G. M. HILLS and ROBERT ROBINSON.

RAPER and WAYNE (*Biochem. J.*, 1928, 22, 188) prepared 10-phenyldecoic acid * (cf. Borsche, *Ber.*, 1919, 52, 2077) and found that when it was administered to dogs the amount recovered in the form of phenaceturic acid was less than that anticipated on the theory of quantitative β-oxidation of the fatty acid chain. The longer the chain in the acids of this series, the closer is the approximation to a normal fatty acid and hence we synthesised the *substances* named in the title with the object of studying the end products of their katabolism.

The synthetic method of Robinson and Robinson (J., 1925, 127, 175) was employed and the condensation products of ethyl sodio-13-keto-12-carbethoxymyristate with β-phenylpropionyl chloride and 10-phenyldecoyl chloride were hydrolysed in stages. The resulting keto-acids, 13-*keto*-15-*phenylpentadecoic acid* and 13-*keto*-22-*phenylbehenic acid*, respectively, were reduced by Clemmensen's method.

* The carboxyl group of the fatty acids is numbered 1.

Experiments with rabbits were carried out with the assistance of Dr. C. P. Stewart in the Department of Chemistry Applied to Medicine of Edinburgh University, and the authors are grateful to Professor G. Barger, F.R.S., for kindly providing the necessary facilities. The physical properties of the sodium salts of the acids, however, rendered them unsuitable for injection, and no evidence for the metabolism of the acids was obtained after feeding by stomach tube. The order of magnitude of the solubility of sodium 15-phenylpentadecoate in water was: 35°, 0·8; 40°, 1·7; 65°, 17·0 g./1000 c.c. Sodium 22-phenylbehenate gave no true aqueous solutions, but formed metastable emulsions containing up to 10—15% of the salt. The p_H was near 10, but could be reduced to about 8 by the addition of bile salt. The more concentrated emulsions set to a translucent gel when kept at room temperature.

Experimental.

13-*Keto-15-phenylpentadecoic Acid*, $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}[CH_2]_{11}{\cdot}CO_2H$.—Ethyl sodio-13-keto-12-carbethoxymyristate (from 34·5 g. of the ester and 2·3 g. of granulated sodium) was prepared in boiling ethereal solution (300 c.c.) and, after cooling, β-phenylpropionyl chloride (17 g.) in ether (20 c.c.) was added. The mixture was kept for 24 hours and then refluxed for an hour; sodium chloride was removed by washing with water, and the solvent evaporated. The residue was shaken with 3% aqueous potassium hydroxide (1000 c.c.) for 12 hours and the products were collected after acidification and refluxed with 5% sulphuric acid (750 c.c.) for 24 hours. The organic products were again isolated and boiled with 3·5% aqueous potassium hydroxide (650 c.c.) for 12 hours. The material now precipitated by acid (air-dried, 32·5 g.) had m. p. 45—52°. Repeated crystallisation of a small specimen from light petroleum, benzene–light petroleum, carbon disulphide, and aqueous methyl alcohol gave a product, m. p. 67°, the carbon content of which was 3% lower than expected. The crude material (45 g.) was therefore crystallised once from light petroleum, affording 31 g., m. p. 61—64°, and phenylpropionic acid (7 g.). The ethyl ester was then prepared and fractionated, yielding (a) 0·5 g., b. p. 130—150°/12 mm., consisting of ethyl β-phenylpropionate; (b) 18 g., b. p. 145—160°/0·5 mm., consisting of ethyl 13-ketomyristate (see below); (c) 12·5 g. of residue, m. p. 33—35°. After saponification the crude acid from the residue had m. p. 60—63° (12 g.) and it separated from benzene eventually as white plates, m. p. 76—77° (Found: C, 75·8; H, 9·7. $C_{21}H_{32}O_3$ requires C, 75·9; H, 9·7%). The yield of ethyl ketomyristate was 46% and that of the *ketophenylpentadecoic acid*, once crystallised from benzene, m. p. 72—74°, was 20%. The *semicarbazone* crystallised from alcohol in irregular prisms, m. p. 87—88° (Found: C, 67·7; H, 8·9; N, 10·6. $C_{22}H_{35}O_3N_3$ requires C, 67·8; H, 9·1; N, 10·8%).

Ethyl 13-*ketomyristate* (above) gave the same semicarbazone as the impure ester obtained by Ruzicka and Stoll (*Helv. Chim. Acta*, 1927, **10**, 691). The ester crystallised from chilled light petroleum in narrow prisms, m. p. 28—29° (Found: C, 71·5; H, 11·1. $C_{16}H_{30}O_3$ requires C, 71·1; H, 11·2%).

15-*Phenylpentadecoic Acid*, $CH_2Ph{\cdot}[CH_2]_{13}{\cdot}CO_2H$.—Reduction of the foregoing keto-acid was effected by Clemmensen's method as modified by Le Sueur and Withers (J., 1915, **107**, 736): amalgamated zinc filings (20 g.) and concentrated hydrochloric acid (100 c.c.) were used to reduce 1 g. of the acid in 70—80 hours at the b. p., and the yield was 94%. The zinc was added in two portions, and the hydrochloric acid in many portions; occasionally the liquid was filtered through glass wool (which was later added to the zinc), and fresh hydrochloric acid employed. The *acid* crystallised from alcohol or light petroleum in white irregular prisms, m. p. 60—61° (Found: C, 79·1; H, 10·9. $C_{21}H_{34}O_2$ requires C, 79·2; H, 10·8%).

13-*Keto-22-phenylbehenic Acid*, $CH_2Ph{\cdot}[CH_2]_8{\cdot}CO{\cdot}[CH_2]_{11}{\cdot}CO_2H$.—10-Phenyldecoic acid (Raper and Wayne, *loc. cit.*) was converted into the chloride, b. p. 204°/14 mm. (some decomp.), by means of thionyl chloride. The *anilide*, obtained from the chloride and aniline, crystallised from aqueous alcohol in colourless needles, m. p. 71—72° (Found: C, 81·8; H, 9·0; N, 4·3. $C_{22}H_{29}ON$ requires C, 81·7; H, 9·0; N, 4·3%). Ethyl phenyldecoate, from the chloride and alcohol, had b. p. 199°/13 mm., 171°/0·3 mm.

The synthesis of the keto-acid followed exactly the lines of that already described, the β-phenylpropionyl chloride being replaced by 10-phenyldecoyl chloride (from 24·8 g. of the acid). The yield of crude acids was 40 g. and the related ethyl esters (32·5 g.) were fractionated, yielding 19 g. of a mixture of ethyl ketomyristate and ethyl phenyldecoate, b. p. 154—162°/0·45 mm., and 8·5 g. of a residue. The latter was hydrolysed, and the *ketophenylbehenic acid*

isolated; it separated from alcohol in white crystals, m. p. 81° (Found: C, 78·2; H, 10·5. $C_{23}H_{46}O_3$ requires C, 78·3; H, 10·8%).

22-*Phenylbehenic Acid.*—The keto-acid (4 g.) was reduced in the same way as ketophenylpentadecoic acid; the product crystallised from acetone in irregular prisms, m. p. 81° (Found: C, 80·7; H, 11·5. $C_{28}H_{48}O_2$ requires C, 80·7; H, 11·6%). Mixed with the keto-acid, m. p. 81°, the depression was only 2°. This *acid* is readily soluble in alcohol, benzene, and warm ethyl acetate, sparingly soluble in cold ethyl acetate, and very sparingly soluble in boiling light petroleum. On a larger scale the crude products of hydrolysis of the ββ'-diketonic ester were reduced by means of amalgamated zinc and hydrochloric acid, and the products esterified and distilled. In this way ethyl myristate, b. p. 140—155°/0·5 mm., and ethyl phenyldecoate, b. p. 170—190°/0·5 mm., could be readily separated and purified by refractionation; the residual *ethyl phenylbehenate* crystallised from alcohol in white prisms, m. p. 53° (Found: C, 80·8; H, 11·8. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%). The yield of crude phenylbehenic acid was about 30%.

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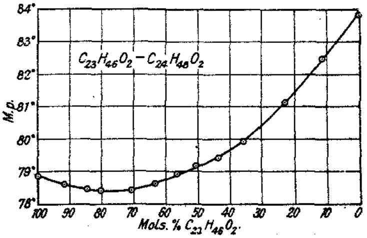
62. *Tricosanoic and Tetracosanoic Acids and Certain Derivatives.*

By R. ASHTON, ROBERT ROBINSON, and J. C. SMITH.

THE identity of the acid obtained by the oxidation of cerebronic acid (Thierfelder, *Z. physiol. Chem.*, 1904, **43**, 21) has been the subject of considerable discussion (Klenk, *ibid.*, 1928, **174**, 214; Taylor and Levene, *J. Biol. Chem.*, 1929, **84**, 23; Klenk and Diebold, *Z. physiol. Chem.*, 1933, **215**, 79; Levene and Heymann, *J. Biol. Chem.*, 1933, **102**, 1); it is agreed that the substance is either *tricosanoic acid* or a mixture containing tetracosanoic acid. We have accordingly synthesised these acids by the method of Robinson and Robinson (J., 1925, **127**, 175; 1930, 745) and carefully characterised the pure substances by determinations of freezing and melting points with the thermometer immersed in the liquid.



The melting-point curve for the system tricosanoic acid–tetracosanoic acid shows that these acids form a continuous series of solid solutions with a minimum (type III, Roozeboom, *Z. physikal. Chem.*, 1899, **30**, 385), there being less than 0·5° difference in melting point between mixtures containing from 0 to 40% of tetracosanoic acid. Mixtures of acids containing an even number of carbon atoms, for example, tetracosanoic and hexacosanoic acids (Piper, Chibnall, and Williams, *Biochem. J.*, 1934, **28**, 2182; compare de Visser, *Rec. trav. chim.*, 1897, **17**, 182), show considerable depressions of melting point. But it has been shown that heptadecoic acid forms type III systems with either palmitic or stearic acid (Shriner, Fulton, and Burks, *J. Amer. Chem. Soc.*, 1933, **55**, 1494), and moreover there is no evidence in the "odd-even" systems of the non-congruent melting points which in the "even-even" systems indicate the existence of some "crystal compound" between the two acids. Thus the "even-odd" acid systems resemble the alcohol

and the hydrocarbon systems (Smith, J., 1931, 802; 1932, 737). A specimen of the oxidation product of cerebronic acid was supplied by Professor Dr. E. Klenk, to whom our warmest thanks are due, but in view of the cryoscopic behaviour of tricosanoic and tetracosanoic acid mixtures it was found impossible to reach a definite conclusion in regard to its identity. It is hoped that an *X*-ray examination will throw more definite light on the matter.

In view of the frequent use of the method of mixed melting points in capillary tubes for the identification of long-chain compounds, it is necessary to point out that the method is often quite unreliable; the present is a clear case in point.

EXPERIMENTAL.

Lauryl Chloride.—Lauric acid was purified by fractionation of its ethyl ester, b. p. 140°/15 mm., followed by crystallisation of the acid recovered after hydrolysis of the middle fraction, to constant m. p. 43·7° (m. p. in a capillary tube, 44·8°). The chloride, b. p. 134°/9—10 mm., was obtained by the use of thionyl chloride.

Ethyl 11-*Bromoundecoate.*—This ester, b. p. 174°/10 mm., was obtained by esterification of the acid prepared by the method of Ashton and Smith (J., 1934, 1308); the difficulties reported by Walker and Lumsden (J., 1901, 79, 1196) were not encountered.

13-*Ketotetracosanoic Acid.*—Acetoacetic ester (19 g.) was added to a cooled solution of sodium (2·7 g.) in the minimum quantity of alcohol. Ethyl 11-bromoundecoate (34 g.) was then added, and the mixture refluxed for 10 hours. The isolated product distilled at 197°/1·1 mm. (yield, 26·5 g. or 66%) (cf. G. M. Robinson, J., 1930, 745).

Sodium (3·5 g.) was granulated and mixed with a solution of the above ester (51 g.) in ether. When the sodium had disappeared, an ethereal solution of lauryl chloride (33 g.) was added. After being kept for 24 hours at room temperature, the mixture was refluxed for 1 hour. The precipitated sodium chloride was removed by washing with water, and the ether evaporated. The residue (75 g.) was shaken for 24 hours with 2·5% sodium hydroxide solution (300 c.c.), and the product isolated by acidification and extraction with ether. After the ether had been removed, 5% sulphuric acid (375 c.c.) was added, and the mixture boiled for 24 hours. The product was isolated in the same manner as before, 5% sodium hydroxide solution (375 c.c.) added, and the mixture boiled for 24 hours, a clear solution being obtained. On acidification an oil separated; this solidified on cooling and was collected (57·5 g.). After four crystallisations from alcohol and two from light petroleum, the *acid* had a constant m. p. 95° (yield, 16 g. or 33%) (Found: C, 75·9; H, 12·0. $C_{24}H_{46}O_3$ requires C, 75·4; H, 12·0%).

Tetracosanoic Acid.—13-Keto-*n*-tetracosanoic acid (5 g.) was reduced by Clemmensen's method (*Ber.*, 1913, 46, 1837; cf. Le Sueur and Withers, J., 1915, 107, 736). The product was extracted with boiling benzene. On cooling, the solution deposited crystals (flat plates), m. p. 83° (yield, 4·5 g. or 95%). Two crystallisations from acetone brought the m. p. to 84° (capillary tube) and this was not changed by two further recrystallisations from benzene (Meyer, Brod, and Soyka, *Monatsh.*, 1913, 34, 1113, give m. p. 85·5—86°; Taylor, *J. Biol. Chem.*, 1931, 91, 541, gives m. p. 84—85°). With the thermometer in the liquid, the acid froze at 82·7° and melted at 82·8°. This specimen was used in preliminary experiments in the system $C_{23}H_{46}O_2$–$C_{24}H_{48}O_2$.

Another specimen, synthesised in the same way, was purified as follows: (1) crystallised from benzene, it softened at 81°, m. p. 82—83° (capillary tube); (2) recrystallised from benzene, it softened and melted 0·5° higher (3 g.); (3) recrystallised from acetone, it softened at 83·5°, m. p. 83—84° (2·55 g.); (4) recrystallised from acetone, no change, m. p. 83·25° (Beckmann apparatus); (5) recrystallised from acetone; (6) recrystallised from acetone, f. p. 83·37°, m. p. 83·70° (2·2 g.); (7), (8) recrystallised from acetone, m. p. 83·8°; (9) recrystallised from *n*-propyl alcohol; (10) recrystallised from acetone, f. p. 83·5°, m. p. 83·8°, m. p. 83·5—84·5° (capillary tube). The acid behaved like a polymorphous substance, a transition occurring near the m. p. (Found: C, 78·4; H, 13·2. Calc. for $C_{24}H_{48}O_2$: C, 78·3; H, 13·0%).

2-*Bromotetracosanoic Acid.*—Dry bromine (4·9 g.) was slowly added to a mixture of molten tetracosanoic acid (3·1 g.) and red phosphorus (0·2 g.). Heating on the steam-bath was continued for 6 hours; an excess of bromine was then still present. The bromo-acid bromide was hydrolysed to the acid, which was collected by means of ether. The product, m. p. 71·5—72°, was recrystallised from light petroleum (yield, 3·2 g. of m. p. 72°, or 85%) (Taylor and Levene, *J. Biol. Chem.*, 1928, 80, 609, give 69·5—70° as the m. p. of α-bromolignoceric acid).

2-Hydroxytetracosanoic Acid.—2-Bromotetracosanoic acid (3 g.) was heated with fused potassium acetate (1·5 g.) and acetic acid (6 c.c.) at 120° for 30 hours. The product was poured into water, collected, washed, and refluxed for 1½ hours with potassium hydroxide (1·5 g.) in alcoholic solution. The acid was precipitated by means of dilute hydrochloric acid and collected. Crystallisation from acetone gave colourless plates, m. p. 96° (yield, 2·2 g. or 85%). Two more crystallisations raised the m. p. to 99·5—100°, unaltered by further recrystallisation from benzene, ethyl alcohol and again from benzene (Taylor and Levene, *loc. cit.*, give 94—95° as the m. p. of α-hydroxylignoceric acid) (Found: C, 75·0; H, 12·5. Calc. for $C_{24}H_{48}O_3$: C, 75·0; H, 12·5%).

Undecoyl Chloride.—Pure undecenoic acid (50 g. of f. p. 24·5°), dissolved in alcohol, was reduced at room temperature in the presence of palladised charcoal. The product (50 g.), crystallised from light petroleum, had m. p. 28·5—29° (Levene and West, *J. Biol. Chem.*, 1914, **18**, 464, give m. p. 29°; Chuit, Boelsing, Hausser, and Malet, *Helv. Chim. Acta*, 1927, **10**, 113, give m. p. 29·5—30·5°). The acid was converted into the acid chloride, b. p. 130°/15 mm., by means of thionyl chloride.

Tricosanoic Acid.—Crude 13-ketotricosanoic acid (19 g.), prepared by substituting undecoyl chloride for lauryl chloride in the above-described synthesis of ketotetracosanoic acid, was reduced by Clemmensen's method, yielding a mixture of tricosanoic and myristic acids (14·5 g.). After three crystallisations from benzene the *tricosanoic acid* had m. p. 78·7° (m. p. in capillary tube, 79·5°) (Found: C, 78·1; H, 12·9. $C_{23}H_{46}O_2$ requires C, 78·0; H, 13·0%). After further crystallisations from benzene and acetone the acid (2·5 g.) had m. p. 79—80·5° (capillary tube), f. p. 78·5°, m. p. 78·6—78·8° (Beckmann apparatus, corr.). It was then recrystallised from pure benzene (100 c.c.) and again from 60 c.c., f. p. 78·60°, m. p. 78·80° (2·3 g.); recrystallised from benzene, m. p. 78·86°; and again from benzene and toluene, f. p. 78·75°, m. p. 78·86° (1·9 g.). The final purifications did not raise the m. p. to a large extent, but the gap between the f. p. and the m. p. was closed and the rate of crystallisation was increased.

Mixtures of Tricosanoic and Tetracosanoic Acids.—The m. p.'s were determined in the Beckmann-type apparatus (cf. Smith, *loc. cit.*), a short Anschütz thermometer being used; in the same apparatus, the f. p.'s were usually 0·05—0·1° lower than the m. p.'s. All the mixtures crystallised readily, and if portions were heated in capillary tubes of the usual size, the whole process of shrinking, softening, and melting occurred over a range of 1·5°.

The m. p.'s observed (see figure) were the following, in which the first figure of each pair recorded shows the mols. % of tricosanoic acid: 100, 78·85°; 91·8, 78·6°; 84·5, 78·45°; 80·1, 78·4°; 70·9, 78·4°; 63·3, 78·6°; 56·5, 78·9°; 50·5, 79·15°; 43·7, 79·4°; 36·0, 79·9°; 22·8, 81·1°; 11·5, 82·45°; 0·0 (100% $C_{24}H_{48}O_2$), 83·8°.

Only a small amount of the oxidation product of cerebronic acid (Klenk) was available and it was not possible to make a comparison with the synthetic acids by the Beckmann technique. A micro-method, however, gave the following results: synthetic tricosanoic acid, m. p. 78·6—78·7°; oxidation product (Klenk), m. p. 77·4—77·8°; a mixture of the foregoing (1 : 1), m. p. 78·0—78·4°. Synthetic tetracosanoic acid, m. p. 82·8°; oxidation product (Klenk), m. p. 77·4—77·8°; a mixture of 2 parts of tetracosanoic acid and 3 parts of the oxidation product had m. p. 78·2—78·5°.

It is not possible to draw definite conclusions from these results, but the oxidation product may be tricosanoic acid still contaminated with an acid of lower molecular weight.

The Dyson Perrins Laboratory, Oxford University. [*Received, December 23rd*, 1935.]

NOTES.

Substituted cyclo*Hexyl Nitrites.* By Louis Hunter and John A. Marriott.

cyclo*Hexyl nitrite* decomposes spontaneously, giving adipic acid, crystals of which begin to be deposited about a week after preparation. Substituted *cyclo*hexyl nitrites, with the few exceptions noted below, are stable for long periods.

The nitrites were prepared by treating the requisite alcohol with a slight excess of aqueous sodium nitrite, followed by the theoretical quantity of sulphuric acid (about 50%), the mixture being thoroughly shaken and cooled. After dilution the nitrite layer (usually at the top) was separated, washed, dried over calcium chloride, and distilled under reduced pressure, the

first fraction being the nitrite. The yield was usually practically theoretical. There was no indication of any separation of 2-, 3-, and 4-substituted *cyclo*hexyl nitrites by fractional distillation into geometrical isomerides.

*cyclo*Hexyl nitrite was a pale yellow liquid with the characteristic odour of organic nitrites; b. p. 31°/10 mm., $d_{4^\circ}^{25^\circ}$ 0·9840, $n_D^{18^\circ}$ 1·4372 (Found: C, 55·7; H, 8·6; N, 10·9; *M* in benzene, 131. $C_6H_{11}O_2N$ requires C, 55·8; H, 8·5; N, 10·8%; *M*, 129). Adipic acid (Equiv., 74·0. Calc., 73·0) separated after 1—4 weeks. Decomposition was most rapid and complete in open vessels, but was not prevented in sealed tubes: these ultimately burst owing to the gaseous pressure generated.

The following nitrites were stable for at least 6 months: 2-*Methyl*cyclo*hexyl nitrite*, b. p. 42°/10 mm., $d_{4^\circ}^{25^\circ}$ 0·9607, $n_D^{14^\circ}$ 1·4402 (Found: C, 58·6; H, 9·3; N, 10·0. $C_7H_{13}O_2N$ requires C, 58·75; H, 9·1; N, 9·8%). 3-*Methyl*cyclo*hexyl nitrite*, b. p. 45°/12 mm., $d_{4^\circ}^{25^\circ}$ 0·9610, $n_D^{13.5^\circ}$ 1·4416 (Found: C, 58·5; H, 9·3; N, 9·7%). 4-*Methyl*cyclo*hexyl nitrite*, b. p. 45°/14 mm., $d_{4^\circ}^{26^\circ}$ 0·9645, $n_D^{14.5^\circ}$ 1·4427 (Found: C, 58·6; H, 9·2; N, 10·0%). 2-*Chloro*cyclo*hexyl nitrite*, b. p. 71°/12 mm., $d_{4^\circ}^{25^\circ}$ 1·1550, $n_D^{12.5^\circ}$ 1·4739 (Found: Cl, 22·6. $C_6H_{10}O_2NCl$ requires Cl, 21·7%). The 1-methyl-, b. p. 46°/12 mm., 2-bromo-, b. p. 87°/10 mm., and 1-ethyl-, b. p. 63°/15 mm., derivatives.

2-Iodo*cyclo*hexyl nitrite, b. p. 110—117° (decomp.)/20—25 mm., rapidly darkened and decomposed after about 7 days into oxides of nitrogen and a black residue free from adipic acid. 1-Phenyl*cyclo*hexyl nitrite decomposed profoundly on distilling at 10 mm.

2-*Bromo*cyclo*hexanol*.—Freshly precipitated mercuric oxide was added (240 g. in 30 g. lots) alternately with bromine (80 g. in 10 g. lots) to well-shaken ice-cold water (800 c.c.) during 90 minutes. The pale yellow solution of hypobromous acid was rapidly filtered, and added in small quantities, with cooling and shaking, to *cyclo*hexene (about 40 g.) until a positive starch-iodide test was obtained. 2-Bromo*cyclo*hexanol was isolated by steam-distillation, dried over anhydrous sodium sulphate, and fractionated under reduced pressure, giving a heavy colourless liquid, b. p. 103—104°/18 mm. (Found: Br, 44·0. Calc.: Br, 44·7%), which, even in the dark, rapidly became pink, red, purple, and finally black. The colour was not removed by washing with thiosulphate. Yield, 30%.

We are indebted to Mr. R. B. Burrows, M.Sc., for some preliminary experiments, and to the Chemical Society for a grant.—UNIVERSITY COLLEGE, LEICESTER. [*Received, November 6th, 1935.*]

The Electrolytic Separation of Deuterium. By A. J. EDWARDS, H. F. WALTON, R. P. BELL, and J. H. WOLFENDEN.

ONE of the characteristic features of the electrolytic separation of the hydrogen isotopes is its lack of reproducibility, which is also reflected in the frequent discrepancies between the results of different investigators. It has not, however, always been clear whether the appropriate correction for loss by evaporation has been applied, or whether the experimental conditions of different workers were truly comparable. Preparatory to a detailed study of the mechanism of the electrolytic separation, we have therefore made experiments to determine whether the minimisation of, and correction for, evaporation loss, together with a general standardisation of the conditions of electrolysis, would eliminate these fluctuations.

Electrolyses of 2% solutions of sodium hydroxide containing 0·5—1% of deuterium oxide were carried out at a variety of cathodes at a *C.D.* of *ca.* 0·25 amp./cm.^{2}, the temperature of the electrolyte being maintained between 25° and 30°. Loss by evaporation and spray was minimised by fitting each cell with an effective condenser, and measured by placing each group of cells in series with a voltameter consisting of an electrolytic cell fitted with drying tubes so that the loss of weight of this cell was due to electrolysis only. The deuterium content of the electrolyte after electrolysis was measured by the flotation-temperature method, the density error being about two parts per million. The resultant error in α, the separation coefficient, is estimated at about 3%.

Various cathodes, specified in the table, were used, and the values of α obtained are tabulated: results with the same series number (denoted by Roman numerals) refer to the same group of cells in series, using identical electrolyte and undergoing the same (minor) fluctuations in temperature and *C.D.*; values of α within the same series therefore correspond to closely comparable conditions.

Cathode.	Electrolytic separation coefficient.	Mean.
Nickel	(I) 4·3, 4·0; (II) 4·8, 4·3, 5·5, 6·2, 6·4	5·1
Copper	(III) 5·9, 6·3, 5·7, 7·0, 5·1, 6·65, 5·8, 7·0	6·2
Arc carbon	(IV) 6·85, 6·3; (V) 4·85, 5·2, 5·7	5·8
Iron	(VI) 10·1, 9·6, 9·2, 8·6, 11·0, 10·2, 10·9	9·9
Nickel coated with sulphide	(VII) 6·3, 6·3, 7·2, 6·7, 6·0, 5·9	6·4
Iron coated with sulphide	(VIII) 8·9, 8·4, 10·9	9·4
Graphite (pure)	(IX) 3·1, 8·9, 4·7, 8·7, 4·7, 3·6	6·7

The variations in α are in every case greater than the most unfavourable estimate of the experimental error. It seems that, in protracted electrolyses under apparently identical conditions, serious fluctuations in the separation coefficient cannot be eliminated. The contrast between iron and the other cathode materials, the extreme variability of α at a graphite cathode, and the effect of a sulphide film on nickel are of interest.

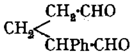
The principal inference to be drawn from these results is that protracted electrolysis experiments are likely to throw very little light on the nature of the electrolytic separation of the isotopes. The observed separation coefficient is likely to be the resultant of several processes, in all of which isotopic discrimination may play a part, and to be further complicated by the partial establishment of the H_2 + DOH = HD + H_2O equilibrium. The most hopeful approach would seem to be electrolyses on a much smaller scale under rigorously controlled conditions, such as have been used in recent studies of overvoltage, together with micro-methods for the analysis of the cathode gas. Such experiments are now in progress in this laboratory.—BALLIOL COLLEGE AND TRINITY COLLEGE LABORATORY, OXFORD. [*Received, November 18th, 1935.*]

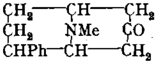
Phenyl-ψ-pelletierine. By B. K. BLOUNT.

DURING the search for suitable dialdehydes to condense to aromatic tropinones (cf. J., 1933, 553) attention was turned to the substituted glutardialdehydes described by Meerwein (*J. pr. Chem.*, 1918, **97**, 225; *Ber.*, 1920, **53**, 1829). Meerwein found that phenylacetaldehyde readily undergoes a sort of Michael addition to Δ^{α}-aldehydes. The primary product, a dialdehyde, was in no case isolated, but was identified after internal disproportioning to the isomeric lactone.

Phenylacetaldehyde and acraldehyde were condensed to α-phenylglutardialdehyde (I), and this was used in the tropinone synthesis, 6-phenylgranatan-3-one (phenyl-ψ-pelletierine) (II) being ultimately obtained and isolated as the *dipiperonylidene* derivative. It is of interest that this complicated tropinone can be built up of *four* substituents by reactions occurring in solution at or below the ordinary temperature. When cinnamaldehyde was substituted for acraldehyde, no trace of a tropinone could be identified.

Meerwein (*loc. cit.*) has shown that certain aliphatic aldehydes also can add on to Δ^{α}-aldehydes. It seemed possible, therefore, that ψ-pelletierine might be synthesised in an analogous way, starting from acetaldehyde and acraldehyde. The reaction gave a basic oil, from which, however, no trace of the characteristic and insoluble dipiperonylidene derivative of ψ-pelletierine could be isolated.

(I.) 

 (II.)

6-Phenylgranatan-3-one.—A solution of phenylacetaldehyde and acraldehyde (3 c.c. of each, both freshly distilled) in methyl alcohol (20 c.c.) was cooled to − 18° and treated drop by drop with a solution of sodium methoxide in methyl alcohol. The first few drops caused no reaction; then reaction suddenly took place and the temperature rose to 15°. After the temperature had again fallen below 0°, the mixture was removed from the freezing-bath and kept at 0° for 16 hours. The solution, containing α-phenylglutardialdehyde, was condensed in the usual way with acetonedicarboxylic acid (5 g.), chalk (6 g.) in water (30 c.c.) and methyl alcohol (20 c.c.) being used, and methylamine (15 c.c. of a 33% aqueous solution) added. After isolation in the usual manner, the mixture of bases was distilled to give an orange-coloured oil (1·5 g.), b. p. 130—210°/15 mm. This was mixed with piperonal (2·5 g.), ethyl alcohol (30 c.c.), and 40% potash solution (0·5 c.c.), and heated on the water-bath for an hour. After cooling, the dark-coloured sticky solid was collected, stirred with acetone, and washed with the same solvent. 2 : 4-*Dipiperonylidene-6-phenylgranatan-3-one* remained as a bright yellow powder, which crystallised from amyl alcohol in spherical aggregates of small yellow needles (0·1 g.), m. p. 210°

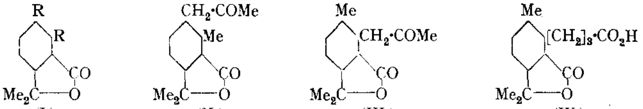
(Found: C, 75·3; H, 5·7; N, 3·3. $C_{31}H_{27}O_5N$ requires C, 75·5; H, 5·5; N, 2·8%). The substance gave with concentrated sulphuric acid the intense royal-blue colour reaction characteristic of dipiperonylidene tropinones.

The author thanks the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, November* 19*th*, 1935.]

63. *Picrotoxin. Part II. Picrotone and Picrotonol.*

By DONALD MERCER and ALEXANDER ROBERTSON.

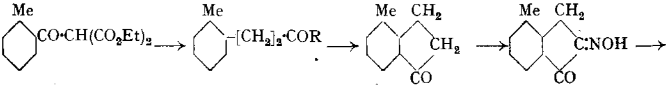
BY the hydrolytic fission of the ketone $C_{14}H_{16}O_3$, formed along with picrotic acid and now named picrotone, Angelico (*Gazzetta*, 1911, **41**, ii, 343; 1912, **42**, ii, 540) obtained acetic acid and a neutral compound which he considered to be α : α : 3 : 4-tetramethylphthalide (I, R = Me), a conclusion in agreement with the oxidation of the ketone to the acid $C_{12}H_{10}O_6$ recently shown to have the structure (I, R = CO_2H) (Part I; J., 1935, 997). The constitution of picrotone was subsequently studied by Horrmann and Bischof (*Arch. Pharm.*, 1921, **259**, 165), who suggested that the compound was represented by formula (II) or (III), a view with which Angelico disagreed (*Gazzetta*, 1923, **53**, 800).



(I.) (II.) (III.) (IV.)

When, however, the experimental results of these authors are taken into account, it follows as a corollary to the structure of picrotic acid (IV),* clearly established in Part I, that picrotone has formula (III).†

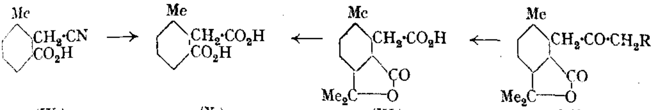
On boiling α-picrotinic acid with 25% sulphuric acid, Angelico (*Gazzetta*, 1910, **40**, i, 391) obtained an α-ketol, $C_{14}H_{16}O_4$, which we have named picrotonol. According to Angelico oxidation of picrotonol gave an acid, $C_{14}H_{16}O_4$, m. p. 165°, devoid of ketonic properties, but Horrmann and Hagendorn (*Arch. Pharm.*, 1921, **259**, 7) considered this to be impossible and stated that the acid had the composition $C_{13}H_{14}O_4$. On repeating this work, we confirmed Horrmann and Hagendorn's observations and found that on decarboxylation the acid $C_{13}H_{14}O_4$ yields the tetramethylphthalide (I, R = Me), identical with a specimen derived from picrotone. Further, in accordance with the behaviour of αα-dimethylphthalides, fission of this monobasic acid with 50% aqueous potassium hydroxide results in the production of acetone and a dibasic acid, $C_{10}H_{10}O_4$, identical with authentic *6-methylhomophthalic acid* (conveniently characterised by conversion into the *anhydride*) synthesised by the following method:



(V.) (VI.) (VII.) (VIII.)

* In formula (VII) of Part I (*loc. cit.*), –CO—CO– should read –CO—O–.

† Evidence for this structure and that of the important related ketol has been deduced by Tettweiler and Drishaus (*Annalen*, 1935, **520**, 163), whose memoir appeared after the completion of the present work, which formed part of a Thesis submitted by one of us (D. M.) for the degree of Doctor of Philosophy of the University of Liverpool in September, 1935. The experimental proofs now recorded differ from those subscribed by these authors, who, it may be noted, have recorded unpublished data from Dissertations submitted to the University of Kiel which have not been available to us.



(IX.) (X.) (XI.) (XII.)

The interaction of *o*-toluoyl chloride and ethyl sodiomalonate yielded the keto-ester (V), which by successive reduction, hydrolysis, and elimination of carbon dioxide gave rise to β-*o*-tolylpropionic acid (VI, R = OH). Cyclisation of the acid chloride (VI, R = Cl) with aluminium chloride in benzene gave 4-methyl-α-hydrindone (VII) in good yield, from which the *oximino*-derivative (VIII) was obtained in the usual manner. By means of *p*-toluene-sulphonyl chloride according to the method of Chakravarti (*J. Indian Chem. Soc.*, 1934, **11**, 105), the last compound was readily transformed into the *acid nitrile* (IX), which on hydrolysis furnished 6-methylhomophthalic acid (X).

That the monobasic acid $C_{13}H_{14}O_4$ must have the structure (XI) clearly follows from its established relationship to the tetramethylphthalide (I, R = Me) and to 6-methyl-homophthalic acid and hence picrotonol must be a primary alcohol having formula (XII, R = OH). Further, since picrotone has been degraded to the phthalide (I, R = Me) and to the acid (I, R = CO_2H) (*loc. cit.*), and since the osazone obtained from picrotonol has been found by us to be identical with the osazone (Horrmann and Bischof, *loc. cit.*) derived from bromopicrotone which is formed from picrotone by the action of sodium hypobromite, therefore bromopicrotone is represented by the structure (XII, R = Br) and picrotone by (III).

Although the studies in progress in these laboratories on the hydrogenation of picro-toxinin and of the hydration products (acids) derived therefrom are not yet complete, it seems desirable in view of the communication by Tettweiler and Drishaus (*loc. cit.*) to record the results obtained from this line of attack which have some bearing on the formation of picrotonol. In accordance with the experiment recorded by these authors we have found that picrotoxinin is readily hydrogenated in acetic acid with hydrogen at atmospheric pressure and a platinum catalyst, forming a dihydro-derivative, m. p. 252°, which we have named α-dihydropicrotoxinin. On treatment with warm 5% sulphuric acid this compound is quantitatively converted into dihydropicrotoxic acid, identical with a specimen obtained from picrotoxic acid by means of a palladium–charcoal catalyst. On the other hand, reduction of picrotoxinin with a palladium–charcoal catalyst in absolute ethyl acetate gives β-*dihydropicrotoxinin*, m. p. 255—256°, which so far we have been unable to hydrate with mineral acids to the corresponding dihydro-acid, but which, like the α-dihydro-derivative, retains the reducing properties exhibited by picrotoxinin. If, however, the reduction with a palladium catalyst (with or without charcoal) is carried out in aqueous alcohol in the presence of small amounts of hydrochloric acid, a mixture is obtained which in the majority of experiments could be crystallised from a small volume of alcohol as an apparently homogeneous compound, m. p. varying from 227° to 232—234°, but which, according to Mr. O'Donnell (private communication), contains at least three compounds. Of special interest is the fact that treatment of this mixture with 2% or 5% sulphuric acid leads to the formation of dihydropicrotoxic acid and picrotonol, being the first recorded production of the latter substance from picrotoxinin. In addition, this result affords an example of the conversion of the hydroaromatic ring system of picrotoxinin into the arom-atic type under milder conditions than have hitherto been possible.

Although picrotoxinin and the majority of its hydration products, as Horrmann's results show (*Annalen*, **1916**, **411**, 273), give unsatisfactory values for hydroxyl estimation by the Zerewitinoff method (*e.g.*, picrotoxinin gives OH, 1·5), the value obtained for picrotoxic acid indicates the presence of an indifferent oxygen atom. This view is confirmed by the properties of *methyl* O-*dimethyldihydropicrotoxate*, which is obtained by the methylation of dihydropicrotoxic acid or its methyl ester by the Purdie method, does not exhibit ketonic properties, and does not react with phosphorus pentachloride or with

thionyl chloride; *the* oxygen atoms are accounted for *thus* : *two in two methoxyl groups*, two in an ester group, two in the lactone group, and one in an oxide ring. Although the changes involved in the conversion of picrotoxinin into picrotoxic acid are still obscure, it is not unlikely that picrotoxinin contains an oxide ring system, because the high result (OH, 1·5) obtained by Horrmann (*loc. cit.*) in the Zerewitinoff determination on this compound is in all probability due to water of crystallisation (approximately $0·5H_2O$) retained by material dried in a vacuum at 100° (see experimental section).

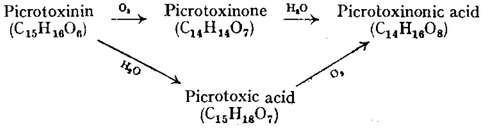
Although on the basis of the *C*-skeleton for picrotic acid and the structure of picrotonol several graphic expressions may be written which can account for some of the main transformations hitherto recorded for picrotoxinin and its hydration products, it must be admitted that sufficient analytical evidence has not so far been published to warrant a choice as a working hypothesis, *e.g.*, step-wise degradation. Nevertheless certain salient points may be usefully commented on at this stage.

(1) In the conversion of picrotoxinin into picrotic acid migration of the carboxyl groups is unlikely and therefore their relative positions may be regarded as fixed. The production of picrotonol from a reduction (?) product under comparatively mild conditions lends support to the *C*-skeleton of picrotoxinin being essentially the same as that of picrotic acid.

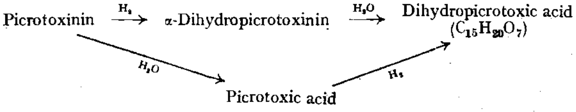
(2) From hydrogenation and ozonisation experiments, picrotoxinin and picrotoxic acid contain only one double bond; prolonged ozonisation of picrotoxinin yields only picrotoxinone. Therefore, on the basis of the *C*-skeleton and if the presence of an oxide ring is accepted, it is probable that these compounds contain a second *C*-ring system, *e.g.*, a bridge of the sabinene or pinene type.

(3) The double bond is present as a vinyl group. Horrmann and his collaborators (*Ber.*, 1916, **49**, 1554; *Arch. Pharm.*, 1920, **258**, 200) maintained that decomposition of the ozonides of picrotoxinin and picrotoxic acid gave only formic acid together with picrotoxinone in one case and picrotoxinonic acid in the other. We, however, have always found that decomposition of these ozonides is also accompanied by the production of formaldehyde, which was isolated as the 2 : 4-dinitrophenylhydrazone in amounts of about 20—25% of that theoretically possible, a result in agreement with the findings of Clemo and MacDonald for the ozonisation of vinyl derivatives (J., 1935, 1294). The formation of formaldehyde in this manner excludes the possibility of picrotoxinin or picrotoxic acid having the group :C:CH—O–.

(4) In the conversion of picrotoxinin into picrotoxic acid the double bond does not appear to be involved, because, as Horrmann (*loc. cit.*) has found, the following scheme holds :



This is corroborated by the fact that a similar scheme holds when the double bond is suppressed by hydrogenation :



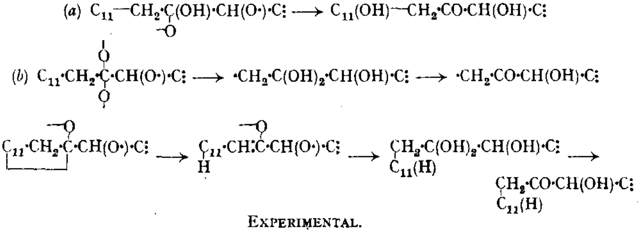
(5) The six oxygen atoms of picrotoxinin are accounted for thus : four in two lactone groups, one as an oxide ring, and one as an alcoholic hydroxyl group, in all probability tertiary. Apart from the two carbonyl oxygen atoms of the lactone groups, the points of

attachment of the hydroxyl, oxide ring, and the potential hydroxyl groups of the lactones have not been determined. It seems reasonably certain, however, that one of the oxygen atoms of the lactone or oxide groups appears as the primary alcoholic group in picrotonol and it is equally probable that the *C*-atom of picrotoxinin appearing in the β-position to the primary alcohol group of picrotonol, *i.e.*, in the γ-position of the picrotoxinin side chain, does not carry an oxygen atom (compare Tettweiler and Drishaus, *loc. cit.*). Further, we are of the opinion that picrotoxinin (and also picrotin) contains a potential keto-group, which under certain conditions, not yet clearly defined, appears as the keto-group of picrotonol and of picrotone. This potential keto-group is in the β-position to a lactone and in the process of conversion into the ketones there is formed at some stage a β-ketonic acid which immediately loses carbon dioxide.

Of the exact nature of this potential keto-group, nothing definite is known. The view has been expressed (compare Tettweiler and Drishaus, *loc. cit.*) that under the influence of acids the keto-group may arise from a potential trihydroxybutyric acid by the following series of changes :

$$\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot C\vdots \longrightarrow \cdot CH{:}C(OH)\cdot CH(OH)\cdot C\vdots \longrightarrow \cdot CH_2\cdot CO\cdot CH(OH)\cdot C\vdots$$

but although this type of change finds analogy in the terpene series in cases where the hydroxyl groups are attached to a ring system, *e.g.*, in the conversion of *p*-menthane-1 : 2 : 4-triol into carvenone (Wallach, *Annalen*, 1893, **277**, 122), we consider this mechanism to be highly improbable in the present instance. Moreover, it does not allow of a conventional explanation of the strong reducing properties exhibited by α- and β-dihydropicrotoxinin as well as picrotoxinin itself in alkaline media. As an alternative we suggest that one or other of the following schemes affords a more satisfactory explanation :



EXPERIMENTAL.

Picrotoxinin.—This was prepared from picrotoxin according to Horrmann and Prillwitz (*Arch. Pharm.*, 1920, **258**, 200). Crystallised from water or alcohol and dried in a vacuum at 100°, it retained water of crystallisation (Found : C, 60·6; H, 5·8. Calc. for $C_{15}H_{16}O_6,0{\cdot}5H_2O$: C, 60·0; H, 5·7%). Anhydrous material was obtained by drying in a high vacuum at 120°/0·1 mm. over phosphoric oxide (Found : C, 61·6, 61·6; H, 5·6, 5·8. Calc. for $C_{15}H_{16}O_6$: C, 61·6; H, 5·5%). The retention of crystal water in this manner may account for Horrmann's failure to obtain analytical results consistent with the now accepted formula for picrotoxinin, which he himself finally adopted (*Ber.*, 1913, **46**, 2793). Meyer and Bruger (*Ber.*, 1898, **31**, 2958) and Bakunin and Giordani (*Rend. Acad. Sci. Fis. Mat. Napoli*, 1924, iii, **30**, 166) also record analytical figures in agreement with the formula $C_{15}H_{16}O_6$.

α : α : 4-*Trimethylphthalide-3-acetic Acid* (XI).—Oxidation of picrotonol was effected by the following modification of Angelico's method (*loc. cit.*) : Concentrated sulphuric acid (13·6 c.c.) was added to a mixture of ketol (6 g.) and water (50 c.c.), and the mixture boiled; a part of the ketol dissolved and the remainder formed a fine suspension. The mixture was diluted with water (25 c.c.), cooled to 0°, and treated with 3% aqueous potassium permanganate (300 c.c.) added during 2 hours with very vigorous stirring, which was then continued for 4 hours. The solution was cleared, and the acid precipitated with excess of sulphur dioxide, forming needles from water, m. p. 165° (Found : C, 66·8; H, 6·0. Calc. for $C_{13}H_{14}O_4$: C, 66·7; H, 6·0%).

A solution of this acid (0·7 g.) in quinoline (40 c.c.) containing Kahlbaum's " Naturkupfer C "

(5 g.) was refluxed for 40 minutes, cooled, mixed with ether (600 c.c.), and filtered. The ethereal solution was freed from quinoline with dilute hydrochloric acid and evaporated, the residue distilled with steam, and the oily product isolated with ether and distilled in a vacuum, giving a fraction (0·3 g.), b. p. 170—180°/18 mm., consisting mainly of α : α : 3 : 4-tetramethylphthalide. Recrystallised from alcohol (charcoal), this compound formed colourless prisms, m. p. 79—80°, identical with a specimen obtained from picrotone according to the directions of Horrmann and Bischof (*loc. cit.*) (Found : C, 75·8; H, 7·4. Calc. for $C_{12}H_{14}O_2$: C, 75·9; H, 7·6%).

β-o-Tolylpropionic Acid.—A solution of *o*-toluoyl chloride (41 g.) in ether (50 c.c.) was gradually added to ethyl sodiomalonate (from 45 c.c. of ethyl malonate and 4·6 g. of sodium) in ether (250 c.c.). One hour later the mixture was refluxed for 1 hour, washed with water, dried, and evaporated, leaving a residue, from which ethyl *o*-toluoylmalonate was obtained by distillation in a high vacuum as a colourless oil (40 g.), b. p. 225°/1 mm., giving a deep red ferric chloride reaction. This ester (5 g.) was boiled with acetic acid containing amalgamated zinc dust (25 g.), ammonium acetate (20 g.), and concentrated hydrochloric acid (75 c.c., added during 4 hours) for 7 hours. The mixture was filtered, the greater part of the acetic acid distilled in a vacuum, and the solution extracted with ether. The residue left on evaporation of the dried extracts was heated at 140° for ½ hour, and the resulting β-*o*-tolylpropionic acid separated from *o*-toluic acid by distillation in a vacuum. The fraction, b. p. 160—170°/20 mm., consisted of almost pure β-*o*-tolylpropionic acid, forming plates, m. p. 104—105°, from water (Young, *Ber.*, 1892, **25**, 2104, gives m. p. 102°).

2-Oximino-4-methyl-1-hydrindone (VIII).—To a cooled solution of β-*o*-tolylpropionyl chloride (prepared from 3·7 g. of the acid with phosphorus pentachloride) in benzene (20 c.c.), aluminium chloride (5 g.) was added in three portions during 40 minutes. 24 Hours later the mixture was refluxed for ½ hour, cooled, and treated with ice and dilute hydrochloric acid. Isolated by steam distillation and subsequent extraction from the distillate with ether, the hydrindone (VII) formed stout needles from light petroleum (b. p. 60—80°), m. p. 103—104° (Found : C, 82·1; H, 6·9. Calc. for $C_{10}H_{10}O$: C, 82·2; H, 6·9%) (Young, *loc. cit.*, gives m. p. 95°).

Concentrated hydrochloric acid (0·5 c.c.) was added to a solution of the hydrindone (2 g.) in alcohol (12 c.c.) and amyl nitrite (4 c.c.), and the mixture kept at 40—50° for 20 minutes. The resulting *oximino*-derivative (VIII) (2 g.) was drained from the alcoholic liquors and recrystallised from alcohol, forming colourless needles, m. p. 215° (decomp.) (Found : N, 8·0. $C_{10}H_9O_2N$ requires N, 8·0%).

6-Methylhomophthalic Acid (X).—(A) *p*-Toluenesulphonyl chloride (3 g.) was added to the yellow solution of the aforementioned oximino-compound (2 g.) in 10% aqueous sodium hydroxide (21 c.c.), and the mixture (agitate) heated to 100° in the course of 10 minutes and then kept at this temperature for a further 7 minutes. The cooled solution was treated with charcoal, filtered, and acidified with hydrochloric acid, yielding *o-tolylacetonitrile-3-carboxylic acid* (2 g.), which separated from water in colourless needles, m. p. 142—143° (Found : N, 7·7. $C_{10}H_9O_2N$ requires N, 8·0%). Hydrolysis of this nitrile (2 g.) with boiling 20% aqueous sodium hydroxide (20 c.c.) for 5 hours gave an almost theoretical yield of *6-methylhomophthalic acid*, which formed needles (2 g.) from water, m. p. 195—196° (Found : C, 62·0; H, 5·4. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·2%).

(B) α : α : 4-Trimethylphthalide-3-acetic acid (2 g.) was heated with 50% aqueous potassium hydroxide (2 c.c.) in a small distilling flask to 300—315° in the course of 15 minutes (temperature, 150° after 5 minutes; 220° after 10 minutes) and then maintained at this temperature for 15 minutes. The acetone, which was completely evolved at 300° in about 10 minutes, was collected and converted into the 2 : 4-dinitrophenylhydrazone, m. p. 128°, identified by comparison with an authentic specimen.

Acidification of a solution of the alkaline residue in water (10 c.c.) with hydrochloric acid precipitated 6-methylhomophthalic acid, which separated from water in needles, m. p. 192—194°, undepressed by admixture with an authentic specimen. Treatment of this material (0·3 g.) with warm acetyl chloride (3 c.c.) for 15 minutes gave rise to the *anhydride* which, after the removal of the acetyl chloride and acetic acid in a vacuum, crystallised from benzene in needles, m. p. 150°, identical with a specimen prepared from the synthetic acid in the same manner (Found : C, 68·0; H, 4·9. $C_{10}H_8O_3$ requires C, 68·2; H, 4·6%).

Ozonisation of Picrotoxinin and of Picrotoxic Acid.—A stream of ozone and oxygen was led into a solution of anhydrous picrotoxinin (2 g.) in chloroform (200 c.c.) for 24 hours; the ozonide gradually separated in colourless prisms. After the removal of the chloroform in a vacuum the solid was decomposed by being heated with water (200 c.c.), and the solution distilled with the addition of more water (200 c.c.) as required. About 300 c.c. of aqueous distillate were collected

and on treatment with excess of 2 : 4-dinitrophenylhydrazine hydrochloride in 2*N*-hydrochloric acid gave a precipitate of formaldehyde-2 : 4-dinitrophenylhydrazone, which was collected 5 hours later, washed, and crystallised from aqueous alcohol, forming orange-yellow needles, m. p. 164—165°, undepressed by admixture with an authentic specimen, m. p. 165—166°. Yield of formaldehyde, *ca.* 20% of the theoretical.

The ozonisation of picrotoxinin (6 g.) was also carried out with absolute ethyl acetate (150 c.c.) as the solvent; the ozonide was decomposed with water (100 c.c.) at room temperature, the precipitate of α-picrotoxinone (5·5 g.) collected, and the formaldehyde isolated from the aqueous liquors by steam distillation and converted into the 2 : 4-dinitrophenylhydrazone, m. p. 164—165°; yield of formaldehyde, *ca.* 20—25% of the theoretical. α-Picrotoxinone was characterised by conversion into the β-form, m. p. 252—253°.

Ozonisation of picrotoxic acid and of methyl picrotoxate was carried out under similar conditions and gave formaldehyde in addition to picrotoxinonic acid and its methyl ester (compare Horrmann and Wächter, *Ber.*, 1916, **49**, 1554).

Hydrogenation of Picrotoxinin with a Platinum Catalyst.—Picrotoxinin (5 g.) was hydrogenated in acetic acid (200 c.c.) with a platinum catalyst and hydrogen at atmospheric pressure; absorption (1 mol.) was complete in about 5 minutes. After isolation, α-dihydropicrotoxinin crystallised from alcohol in colourless plates, m. p. 252°, $[\alpha]_D^{20°}$ − 4·02° in acetone (Found: C, 61·2; H, 6·1. Calc. for $C_{15}H_{18}O_6$: C, 61·2; H, 6·1%). This compound (1 g.) was recovered unchanged after treatment with acetic anhydride (4 c.c.) and pyridine (2 c.c.) at room temperature for 10 days.

α-Dihydropicrotoxinin (2 g.) was refluxed with 5% sulphuric acid (100 c.c.) for 20 hours, and the mixture was neutralised with sodium bicarbonate and extracted with ether. Evaporation of the extracts left only slight traces of a residue. Acidification of the aqueous liquors with hydrochloric acid gave dihydropicrotoxic acid, which was isolated with ether and crystallised from ethyl acetate, forming slender needles (1·5 g.), m. p. 252—253°, identical with a specimen obtained by the reduction of picrotoxic acid in water with a palladium–charcoal catalyst (Horrmann and Wächter, *loc. cit.*).

Hydrogenation of Picrotoxinin with a Palladium Catalyst.—(A) By means of a catalyst prepared from palladium (0·3 g.) and charcoal (2 g.) in the usual manner and carefully washed with much water, alcohol, and ethyl acetate, picrotoxinin (5 g.) was hydrogenated in absolute ethyl acetate (200 c.c.) with hydrogen at atmospheric pressure (approximately 400 c.c. absorbed; theoretical for one double bond, 360 c.c.). After isolation, *β-dihydropicrotoxinin* separated from ethyl acetate in prismatic needles, m. p. 256—257°, $[\alpha]_D^{20°}$ − 24·69° in acetone (Found: C, 61·2; H, 6·1%). This compound was recovered unchanged after having been refluxed with 5% sulphuric acid for 24 hours. A mixture of α- and β-dihydropicrotoxinin melted at about 220—225°.

(B) Hydrogen was led into a well-agitated solution of picrotoxinin (5 g.) in alcohol (300 c.c.) and water (100 c.c.) containing palladium chloride (0·4 g.), 2*N*-hydrochloric acid (1 c.c.), and active charcoal (2 g.). Absorption was rapid at first but had almost ceased when, after 2 hours, approximately the theoretical amount of hydrogen for one donble bond had been absorbed. The filtered solution was evaporated in a vacuum to about 25 c.c., and the product precipitated with water; the m. p. varied from 227° to 232°; yield, *ca.* 4·5 g. This material could be crystallised from a small volume of alcohol, forming prisms, apparently homogeneous, the m. p. varying with individual preparations from 227° to 234°.

A solution of this product (1 g.) in methyl alcohol containing potassium hydroxide (0·2 g.) was kept for 10 minutes and then evaporated in a vacuum. The residue was dissolved in a small volume of water, neutralised with hydrochloric acid, and extracted with ether. Evaporation of extracts left a product, from which methyl dihydropicrotoxate was isolated by crystallisation from ethyl acetate, m. p. 210°, identical with that of an authentic specimen (Horrmann and Wächter, *loc. cit.*, give m. p. 205°) (Found: C, 58·8; H, 6·8. Calc. for $C_{16}H_{22}O_7$: C, 58·9; H, 6·8%).

Picrotonol.—The material (5 g.), m. p. 228—232°, was boiled with 5% (or 2%) sulphuric acid (200 c.c.) for 18—20 hours, and the cooled solution was filtered from a small amount of crystalline solid, m. p. 255—256° (identified as β-dihydropicrotoxinin), neutralised with sodium bicarbonate, and extracted with ether. Evaporation of the dried extracts left crude picrotonol as a pale brown oil (2—3 g.). Extraction of the aqueous liquors which had been acidified with hydrochloric acid gave dihydropicrotoxic acid, m. p. 252—253° after purification from ethyl acetate.

The crude ketol was converted into the semicarbazone, which separated from alcohol in prisms, m. p. 224—226° (Found: C, 58·8; H, 6·2; N, 13·9. Calc. for $C_{15}H_{19}O_4N_3$: C, 59·0;

H, 6·2; N, 13·8%). This derivative was identical with material prepared from authentic ketol obtained from α-picrotinic acid * with 40% sulphuric acid (Horrmann, *loc. cit.*), m. p. and mixed m. p. 224—226°. Decomposition of the semicarbazone (2 g.) with a boiling solution of oxalic acid (2 g.) in water (20 c.c.) during 2 hours gave pure picrotonol, obtained on isolation with ether as a viscous syrup which did not crystallise. On being boiled with 17% acetic acid (70 c.c.) and phenylhydrazine (5 c.c.) for 2 hours, the ketol (1 g.) yielded the osazone, forming golden rods from much alcohol, m. p. 202°, identical with an authentic specimen (Found: C, 73·1; H, 6·4; N, 13·4. Calc. for $C_{26}H_{26}O_2N_4$: C, 73·2; H, 6·1; N, 13·1%). The same osazone was obtained from bromopicrotone by Horrmann and Bischof's method (*loc. cit.*).

A solution of picrotonol (1 g.) and *p*-nitrobenzoyl chloride (2 g.) in pyridine (15 c.c.) was kept at about 70° for 2 days and then mixed with ice-water and excess of dilute hydrochloric acid. The solid was washed with water and thoroughly extracted with aqueous sodium bicarbonate and then with cold water. Crystallised from alcohol, the residual p-*nitrobenzoate* formed slender needles, m. p. 155°, identical with a specimen obtained from authentic ketol by the same method (Found: C, 63·3; H, 4·8; N, 3·7. $C_{22}H_{19}O_7N$ requires C, 63·5; H, 4·8; N, 3·5%).

Picrotonol was also obtained directly from picrotin by the procedure which Horrmann used for the preparation of the compound from α-picrotinic acid; semicarbazone, m. p. and mixed m. p. 224—225°.

Methyl O-*Dimethyldihydropicrotoxate.*—Dihydropicrotoxic acid (6 g.) was methylated in boiling methyl alcohol (150 c.c.) with excess of methyl iodide and silver oxide, gradually added during 24 hours. The product was isolated and the process repeated (three or four times) without the addition of methyl alcohol, until a product was obtained which was unchanged on further treatment. The *compound* (6 g.) crystallised from methyl alcohol or light petroleum (b. p. 80—100°) in needles, m. p. 146—147°, $[\alpha]_D^{20°}$ + 95·93° in chloroform [Found: C, 61·1; H, 7·5; OMe, 26·6. $C_{15}H_{17}O_4(OMe)_3$ requires C, 61·1; H, 7·3; OMe, 26·2%]. The same ether was obtained by methylation of methyl dihydropicrotoxate by the same procedure. Though it did not appear to be readily hydrolysed with alcoholic potassium hydroxide, the compound (0·4 g.), on being boiled with hydrazine hydrate (10 c.c.) for 2 hours, gave rise to O-*dimethyldihydropicrotoxic acid*, forming needles from water, m. p. 206—207° [Found: C, 59·6; H, 7·2; OMe, 17·6. $C_{15}H_{18}O_5(OMe)_2$ requires C, 60·0; H, 7·1; OMe, 17·9%].

Methyl *O*-dimethyldihydropicrotoxate was recovered unchanged after having been refluxed with excess of thionyl chloride or with phosphorus pentachloride in chloroform.

APPENDIX.

For 5-methyl-α-tetralone, Tettweiler and Drishaus (*loc. cit.*) give m. p. 63°, but we have always found the m. p. of the synthetic compound to be 50—51° in agreement with Heilbron and his collaborators (J., 1930, 425). Decomposition of the semicarbazone, m. p. 245—246° (for this derivative, Tettweiler and Drishaus give m. p. 242°), with hot aqueous oxalic acid regenerated the tetralone, m. p. 50—51°, unchanged after purification by steam distillation, distillation in a vacuum, and repeated crystallisation from light petroleum (b. p. 40—60°) and aqueous acetic acid.

The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of them (D. M.).

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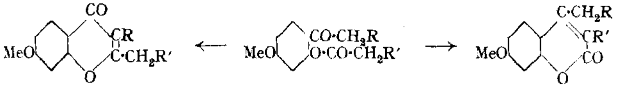
* In order to avoid confusion with picrotic acid (Part I, *loc. cit.*) the monobasic acids from picrotin should be named α- and β-picrotinic acid (*Abstracts*, 1910, **98**, i, 404; 1913, **104**, i, 70; 1916, **110**, i, 566) and not α- and β-picrotic acid (*Abstracts*, 1912, **102**, i, 1008).

64. *Studies in the Pyrone Series. Part III. The Influence of the Phenyl Group in the Kostanecki Reaction.*

By I. M. Heilbron, D. H. Hey, and B. Lythgoe.

Previous work has revealed that the Kostanecki reaction cannot be used as a general method for the synthesis of chromones and naphtha-γ-pyrones (Heilbron, Heslop, and Howard, J., 1933, 1263), since it may produce a chromone, a coumarin, or a mixture of both. It may be presumed that, in the reaction between an *o*-hydroxyphenyl ketone and a mixture of the anhydride and the sodium salt of a fatty or substituted fatty acid, the initial stage involves the formation of an *O*-acyl ketone (I) (compare Baker, J., 1933, 1381), which can lose water in one of two ways, to give either the chromone (II) or the coumarin (III).



(II.) (I.) (III.)

The course of the reaction has been shown to be dependent not only on the acid anhydride and the salt used, but also on the nature of the *o*-hydroxyphenyl ketone (Heilbron, Hey, and Lythgoe, J., 1934, 1581); replacement of sodium acetate and acetic anhydride by the corresponding derivatives of propionic or butyric acid favours coumarin formation, and an ethyl ketone (R = Me) shows a far greater disposition towards the formation of chromones than does the corresponding methyl ketone (R = H).

In further experiments on the mechanism of the Kostanecki reaction, the influence of a phenyl group (a) in the sodium salt and the anhydride of the fatty acid and (b) in the side chain of the ketone has been examined, by the methods previously described (compare Heilbron, Hey, and Lythgoe, *loc. cit.*), with regard to the production of both chromone and coumarin.

Derivatives of phenylacetic acid have already been employed by other workers, but in most cases under complicated conditions. For example, both Bargellini and Venkataraman frequently use a mixture of sodium phenylacetate and acetic anhydride; although in specific cases the use of such a mixture may afford the best means for the preparation of a particular pyrone, its employment in any attempt to elucidate the mechanism of the reaction is of doubtful value. Prolonged boiling of sodium phenylacetate with acetic anhydride must lead to the formation of some sodium acetate and phenylacetic anhydride as well as possibly the mixed anhydride. By the action of the above mixture on *o*-hydroxyacetophenone (Mahal and Venkataraman, J., 1933, 617), resacetophenone (Bargellini, *Gazzetta*, 1925, **55**, 945; *Atti R. Accad. Lincei*, 1925, **2**, 261), respropiophenone (Chadha, Mahal, and Venkataraman, J., 1933, 1462), and 2-acetyl-1-naphthol (Bargellini, *Atti R. Accad. Lincei*, 1925, **2**, 261; Cheema and Venkataraman, J., 1932, 918) 3-phenylcoumarins were obtained, but when the same mixture was used on 2-propionyl-1-naphthol, 2-phenylacetyl-1-naphthol, and 1-phenylacetyl-2-naphthol (Chadha, Mahal, and Venkataraman, *loc. cit.*) the products were the same chromones as are obtained when a mixture of sodium acetate and acetic anhydride is used. In the latter cases, therefore, the sodium phenylacetate plays no apparent part in the reaction. Baker and Eastwood (J., 1929, 2906) made a similar observation on the action of a mixture of sodium phenylacetate and acetic anhydride on 2 : 4-dihydroxyphenyl benzyl ketone, the product being a 3-phenyl-2-methylchromone, but when the acetic anhydride was replaced by phenylacetic anhydride the anticipated 3-phenyl-4-benzylcoumarin was formed. In the present investigation, therefore, the acid of the sodium salt used is always the same as that of the anhydride.

It has now been found that when either 2-hydroxy-4-methoxyacetophenone or 2-hydroxy-4-methoxypropiophenone is heated with sodium phenylacetate and phenylacetic anhydride the product has almost exclusively the coumarin structure, the compounds

formed being 7-methoxy-3-phenyl-4-methylcoumarin (III; R = H, R′ = Ph) and *7-methoxy-3-phenyl-4-ethylcoumarin (III; R = Me, R′ = Ph)* respectively, although with the latter ketone a small quantity of the isomeric chromone, *7-methoxy-2-benzyl-3-methylchromone (II; R = Me, R′ = Ph)*, also was isolated.

The products of these reactions were identified, if coumarins, both by degradation and by synthesis; *e.g.*, 7-methoxy-3-phenyl-4-methylcoumarin on ring fission and methylation yielded 2 : *4-dimethoxy-α-phenyl-β-methylcinnamic acid*, and similar treatment of 7-methoxy-3-phenyl-4-ethylcoumarin gave 2 : *4-dimethoxy-α-phenyl-β-ethylcinnamic acid*. The synthesis of the two coumarins was effected by condensation of α-acetyl- and α-propionylphenylacetonitrile severally with resorcinol in the presence of sulphuric acid and subsequent methylation. 7-Hydroxy-3-phenyl-4-ethylcoumarin has been prepared by Chadha, Mahal, and Venkataraman (*loc. cit.*) by hydrolysis of the product obtained by heating respropiophenone with sodium phenylacetate and acetic anhydride. A repetition of this experiment gave a product identical with that obtained on demethylation of 7-methoxy-3-phenyl-4-ethylcoumarin, although the melting point of both specimens (268°) was somewhat higher than that given by the above authors (254°). The two isomeric chromones, which could arise from the above Kostanecki reactions, were also synthesised by an unambiguous method. Condensation of 2 : 4-dimethoxyacetophenone with ethyl phenylacetate in the presence of sodium gave 2 : *4-dimethoxy-ω-phenylacetylacetophenone*, which on ring closure yielded *7-methoxy-2-benzylchromone* (II; R = H, R′ = Ph), and methylation of 2 : 4-dimethoxy-ω-phenylacetylacetophenone gave 2 : 4-dimethoxy-α-phenylacetylpropiophenone, which on ring closure gave 7-methoxy-2-benzyl-3-methylchromone (II; R = Me, R′ = Ph) identical with the chromone isolated from the action of sodium phenylacetate and phenylacetic anhydride on 2-hydroxy-4-methoxypropiophenone.

On the other hand, the action of the sodium salt and the anhydride of both acetic and propionic acid on 2-hydroxy-4-methoxyphenyl benzyl ketone gives rise to almost exclusive chromone formation, the products being 7-methoxy-3-phenyl-2-methylchromone (II; R = Ph, R′ = H) and *7-methoxy-3-phenyl-2-ethylchromone* (II; R = Ph, R′ = Me) respectively. These results are in agreement with previous applications of the Kostanecki reaction to benzyl ketones (Baker and Robinson, J., 1925, **127**, 1984; Cheema and Venkataraman, *loc. cit.*; Chadha, Mahal, and Venkataraman, *loc. cit.*). An unambiguous synthesis of these two chromones from 2-hydroxy-4-methoxyphenyl benzyl ketone and ethyl acetate or propionate in the presence of sodium was attempted but without success. It was possible, however, to obtain a *methylenedioxystyryl* derivative of 7-methoxy-3-phenyl-2-methylchromone. Further, the melting point of this chromone agrees with that of the product obtained by methylation of 7-hydroxy-3-phenyl-2-methylchromone (Baker and Robinson, *loc. cit.*). The latter compound, obtained from the action of sodium acetate and acetic anhydride on 2 : 4-dihydroxyphenyl benzyl ketone, must have the γ-pyrone structure, since it is not identical with 7-hydroxy-4-benzylcoumarin obtained from resorcinol and ethyl γ-phenylacetoacetate in the presence of sulphuric acid (Sonn and Litten, *Ber.*, **1933**, **66**, 1518), which is the isomeric coumarin that could arise from the above reaction.* With regard to the corresponding 2-ethylchromone, no styryl derivative could be prepared (compare Heilbron, Hey, and Lowe, J., **1934**, **1311**), but a consideration of all the known facts leaves little doubt as to the validity of the structure suggested.

These results are entirely in agreement with theoretical prediction, since in each case it is the hydrogen at the reactive methylene group between phenyl and carbonyl which takes part in the ring closure. This influence is sufficiently powerful to outweigh the weaker

* The ethyl γ-phenylacetoacetate of Attwood, Stevenson, and Thorpe (J., **1923**, **123**, 1762) is now stated to be ethyl α-phenylacetoacetate (Sonn and Litten, *loc. cit.*). Its use by Baker and Robinson (*loc. cit.*) in condensation with resorcinol in the presence of sulphuric acid therefore gives rise to 7-hydroxy-3-phenyl-4-methylcoumarin (m. p. 225—226°), a compound previously prepared by Jacobson and Ghosh (J., 1915, **107**, 1053), and not 7-hydroxy-4-benzylcoumarin. The preparation of the latter by Sonn and Litten gives rise to a product (m. p. 214—215°), which is apparently identical neither with Hannach and Kostanecki's 7-hydroxy-2-benzylchromone (m. p. 183°; *Ber.*, 1902, **35**, 867) nor with Baker and Robinson's 7-hydroxy-3-phenyl-2-methylchromone (m. p. 240°). The arguments used by Baker and Robinson therefore remain unaffected.

effects introduced either by replacing the methyl ketone by the ethyl ketone, or by using derivatives of propionic acid in place of those of acetic acid. The influence of the phenyl group on the course of the Kostanecki reaction, though more powerful, *is in the same direction* as that of the methyl group. When substituted in the sodium salt and the acid anhydride, both groups favour coumarin formation, but when substituted in the hydroxyacetophenone side chain both groups favour chromone formation.

Note on the Action of Sodium Propionate and Propionic Anhydride on 2-Hydroxy-4-methoxyacetophenone.—This action (Heilbron, Hey, and Lythgoe, *loc. cit.*) is stated to have given 7-methoxy-3 : 4-dimethylcoumarin, together with a small quantity of a second compound, m. p. 81—82°, which gave the correct analysis for the isomeric chromone but was erroneously stated to depress the melting point of 7-methoxy-2-ethylchromone (m. p. 81°; Heilbron, Hey, and Lowe, *loc. cit.*). Repetition of this reaction has shown that the compound of m. p. 81—82° is in fact the latter chromone. The condensation of 2-hydroxy-4-methoxyacetophenone with ethyl propionate in the presence of sodium has also been re-examined and found to yield 5-methoxy-2-propionoacetylphenol, m. p. 83·5° (and not 101° as erroneously reported previously), identical with the diketone obtained from 7-methoxy-2-ethylchromone on ring fission.

EXPERIMENTAL.

Phenylacetic Anhydride.—The following method gave good results: phenylacetic acid (50 g.) and acetic anhydride (150 g.) were boiled in a flask fitted with a Lapworth column, which was jacketed by vapour from boiling acetic acid. The temperature at the head of the column was maintained at 116—120° and after 4 hours 30 c.c. of distillate had been collected, the greater portion of which boiled below 120°. After removal of the excess of acetic anhydride under reduced pressure, the residual phenylacetic anhydride solidified. On crystallisation from light petroleum (b. p. 80—100°) colourless needles were obtained, m. p. 72° (yield, 35 g.).

Action of Sodium Phenylacetate and Phenylacetic Anhydride on 2-Hydroxy-4-methoxyacetophenone.—Sodium phenylacetate (20 g.), phenylacetic anhydride (30 g.), and 2-hydroxy-4-methoxyacetophenone (15 g.) were heated together under reflux at 180° for 8 hours. The product was poured into water and distilled with steam to remove unchanged reactants. An ethereal extract of the residue, after being washed with aqueous alkali to remove traces of 2-hydroxy-4-methoxyacetophenone and dried, deposited 7-methoxy-3-phenyl-4-methylcoumarin which on recrystallisation from alcohol separated in colourless needles (12 g.), m. p. 106·5° (Found: C, 76·4; H, 5·5. Calc. for $C_{17}H_{14}O_3$: C, 76·7; H, 5·3%).

The coumarin gave no depression in melting point on admixture with a specimen prepared by the action of α-acetylphenylacetonitrile on resorcinol in the presence of sulphuric acid (Ghosh, J., 1916, **109**, 109; compare also Baker and Robinson, *loc. cit.*), with subsequent methylation as follows: the hydroxy-coumarin (m. p. 225°, 1·6 g.) was dissolved in dry acetone (75 c.c.) and boiled under reflux for several hours with the addition of methyl iodide (0·5 c.c.) and potassium carbonate (1 g.) (compare Robertson, Robinson, and Struthers, J., 1928, 1457). After removal of solvent, water was added, and the separated solid collected, dissolved in alcohol, boiled with charcoal and filtered. The 7-methoxy-3-phenyl-4-methylcoumarin (1·3 g.) separated in long needles, m. p. 106·5°. Chakravarti (*J. Indian Chem. Soc.*, 1931, **8**, 136) gives m. p. 104°.

A portion of the coumarin was subjected to hydrolytic fission by the method of Canter and Robertson (J., 1931, 1875). The coumarin (4 g.) was boiled under reflux with 20% aqueous sodium hydroxide (50 c.c.) and methyl alcohol (50 c.c.) for about 2 hours, until no turbidity was observed on dilution of a test portion. After the addition of more alkali (30 c.c.) and methyl alcohol (30 c.c.) the cold solution was treated with methyl sulphate (35 c.c.), added in small quantities with frequent shaking. More alkali was then added, and the solution boiled under reflux to hydrolyse any methyl ester formed. The product precipitated on acidification was treated with sodium bicarbonate solution, which left a residue (2 g.) of unchanged coumarin re-formed from hydroxycinnamic acid which had escaped methylation. Acidification of the bicarbonate solution precipitated 2 : *4-dimethoxy-α-phenyl-β-methylcinnamic acid* (2·2 g.), which separated from dilute acetic acid in colourless needles, m. p. 153·5° (Found: C, 72·3; H, 5·95. $C_{18}H_{18}O_4$ requires C, 72·4; H, 6·0%).

Evaporation of the ethereal mother-liquor from which the coumarin had separated left an oil (2 g.), which was kept over-night in presence of alcoholic sodium ethoxide (1 g. of sodium in

60 c.c. of alcohol). The resulting solution was diluted with water, washed with ether, and acidified with acetic acid. The oil precipitated was extracted with ether and washed with aqueous sodium hydroxide. Acidification of the aqueous alkaline solution produced only a slight cloudiness, indicating the almost complete absence of any hydroxydiketone and hence of chromone. Evaporation of the ethereal extract yielded a further quantity of 7-methoxy-3-phenyl-4-methylcoumarin (1·8 g.).

7-Methoxy-2-benzylchromone.—A solution of 2 : 4-dimethoxyacetophenone (13 g., m. p. 40°) (Perkin, Robinson, and Turner, J., 1908, **93**, 1108) in ethyl phenylacetate (35 g., b. p. 227°) (Volhard, *Annalen*, 1897, **296**, 2, footnote) was added to powdered sodium (1·75 g.). The reaction was at first controlled by cooling in ice and then completed by heating on the steam-bath for ½ hour. When cold, ether was added and the granular sodium salt which slowly separated was collected and washed with ether. A portion (4 g.) was dissolved in glacial acetic acid (15 c.c.), and on addition of water the free diketone separated as an oil, which solidified. On crystallisation from methyl alcohol *2 : 4-dimethoxy-ω-phenylacetylacetophenone* (2·5 g.) separated in faintly yellow crystals, m. p. 91° (Found : C, 71·9; H, 5·8. $C_{18}H_{18}O_4$ requires C, 72·4; H, 6·0%). After the diketone (1·5 g.) had been boiled for 15 minutes with glacial acetic acid (20 c.c.) and hydrobromic acid (3 c.c., *d* 1·47), and the solution poured into dilute aqueous alkali, the precipitated *7-methoxy-2-benzylchromone* was extracted with ether; it crystallised from dilute acetic acid in colourless needles, m. p. 192° (Found : C, 76·1; H, 5·7. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%).

Action of Sodium Phenylacetate and Phenylacetic Anhydride on 2-Hydroxy-4-methoxypropiophenone.—The reaction between sodium phenylacetate (15 g.), phenylacetic anhydride (30 g.), and 2-hydroxy-4-methoxypropiophenone (10 g.) was carried out as described above for the corresponding reaction with 2-hydroxy-4-methoxyacetophenone. The product was treated in a similar manner, evaporation of the ethereal solution yielding large colourless crystals of *7-methoxy-3-phenyl-4-ethylcoumarin* (7 g.), which after recrystallisation from alcohol melted at 115° (Found : C, 77·4; H, 5·7. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7%). A portion of the coumarin (1 g.) was demethylated by heating on the steam-bath for 2 hours with a mixture (20 c.c.) of equal parts of hydriodic acid (*d* 1·7) and glacial acetic acid. The solution was poured into dilute sodium carbonate solution and extracted with ether. The ethereal extract was washed with sodium thiosulphate solution, the solvent evaporated, and the residual 7-hydroxy-3-phenyl-4-ethylcoumarin crystallised from alcohol, forming colourless needles (0·3 g.), m. p. 268° (compare Chadha, Mahal, and Venkataraman, *loc. cit.*). A further portion of the coumarin (2 g.) was subjected to hydrolytic fission by the method previously described for 7-methoxy-3-phenyl-4-methylcoumarin, giving unchanged coumarin (0·6 g.) and *2 : 4-dimethoxy-α-phenyl-β-ethylcinnamic acid* (0·9 g.), which crystallised from dilute acetic acid in colourless needles, m. p. 137° (Found : C, 73·0; H, 6·4. $C_{19}H_{20}O_4$ requires C, 73·0; H, 6·4%).

Evaporation of the ethereal mother-liquor from which the coumarin had separated yielded an oil (2·5 g.), to which was added an alcoholic solution of sodium ethoxide (1·5 g. of sodium in 70 c.c. of alcohol). After 12 hours, addition of water precipitated an oil, which was extracted with ether. The crude chromone obtained on removal of the solvent crystallised from alcohol in colourless needles (0·8 g.) of *7-methoxy-2-benzyl-3-methylchromone*, m. p. 102·5° (Found : C, 77·1; H, 5·8. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7%). Acidification of the alkaline layer with acetic acid precipitated an oil, an ethereal extract of which was washed with aqueous sodium hydroxide. Only a minute quantity of oil was liberated on acidification of the alkaline washings, but evaporation of the ethereal extract yielded a further quantity (1·5 g.) of 7-methoxy-3-phenyl-4-ethylcoumarin.

α-Propionylphenylacetonitrile was prepared by the method of Dimroth and Feuchter (*Ber.*, 1903, **36**, 2242) and obtained in colourless needles (from aqueous alcohol), m. p. 61—62°. The above authors record m. p. 70°, and Walther and Schickler (*J. pr. Chem.*, 1897, **55**, 344), using a similar method, obtained a product, m. p. 58°.

7-Methoxy-3-phenyl-4-ethylcoumarin.—To an intimate mixture of α-propionylphenylacetonitrile (3 g.) and resorcinol (2·2 g.) was added, drop by drop, concentrated sulphuric acid (8·5 c.c.). After standing over-night, the yellowish crystalline mass was poured on ice, and the separated solid boiled under reflux with 10% sulphuric acid (100 c.c.). The separated 7-hydroxy-3-phenyl-4-ethylcoumarin (3·6 g.) was washed with water; it crystallised from alcohol in fine needles, m. p. 268°. The hydroxycoumarin (0·8 g.) was methylated by boiling under reflux for 16 hours with acetone (200 c.c.), methyl iodide (2 c.c.), and potassium carbonate (4 g.). After removal of solvent the addition of water precipitated 7-methoxy-3-phenyl-4-ethylcoumarin (0·6 g.), which crystallised from aqueous methyl alcohol in colourless needles, m. p. 115°, not

depressed by the coumarin obtained by the action of sodium phenylacetate and phenylacetic anhydride on 2-hydroxy-4-methoxypropiophenone.

7-Methoxy-2-benzyl-3-methylchromone.—The sodium salt of 2 : 4-dimethoxy-ω-phenylacetylacetophenone (10 g.), prepared as described above, was boiled under reflux for 6 hours with acetone (150 c.c.) and methyl iodide (5 c.c.). After removal of solvent and addition of water, the product was extracted with ether, evaporation of which gave a viscous non-crystallisable oil. A portion (1 g.) was boiled for 10 minutes with glacial acetic acid (50 c.c.) containing hydrobromic acid (2·5 c.c., *d* 1·47). The cold solution was poured into dilute aqueous alkali, from which ether extracted a dark tarry material. The solution obtained by trituration with light petroleum and decantation from insoluble resinous matter deposited 7-methoxy-2-benzyl-3-methylchromone, which on recrystallisation from the same solvent gave colourless needles (0·7 g.), m. p. 102·5°, not depressed by the chromone isolated from the action of sodium phenylacetate and phenylacetic anhydride on 2-hydroxy-4-methoxypropiophenone.

2-Hydroxy-4-methoxyphenyl Benzyl Ketone.—2 : 4-Dihydroxyphenyl benzyl ketone (22·8 g., m. p. 114°) (Chapman and Stephen, J., 1923, **123**, 406), methyl iodide (14·2 g.), and potassium carbonate (13 g.) were boiled under reflux for 12 hours with acetone (200 c.c.). After evaporation of the acetone and addition of water, the separated solid was collected, washed with water, and crystallised from 95% alcohol, giving 2-hydroxy-4-methoxyphenyl henzyl ketone (22 g.) in colourless needles, m. p. 90°. Tambor's method (*Ber.*, 1910, **43**, 1884) gave less satisfactory yields.

Action of Sodium Acetate and Acetic Anhydride on 2-Hydroxy-4-methoxyphenyl Benzyl Ketone.—The product of heating 2-hydroxy-4-methoxyphenyl benzyl ketone (9 g.), sodium acetate (25 g.), and acetic anhydride (35 g.) for 5 hours at 160° was treated as in the previous Kostanecki reactions. Partial evaporation of the ethereal solution caused deposition of 7-methoxy-3-phenyl-2-methylchromone (6·8 g.), which separated from 95% alcohol in long needles, m. p. 136° (compare Baker and Robinson, *loc. cit.*) (Found : C, 76·7; H, 5·7. Calc. for $C_{17}H_{14}O_3$: C, 76·7; H, 5·3%). Evaporation of the ethereal mother-liquor left a brown oil, which, after standing over-night with alcoholic sodium ethoxide (2 g. of sodium in 100 c.c. of alcohol), was poured into water. Extraction with ether yielded a further quantity of 7-methoxy-3-phenyl-2-methylchromone (1·6 g.). The aqueous alkaline layer was acidified with acetic acid and extracted with ether. The ethereal extract was washed with aqueous sodium hydroxide and after removal of solvent the residual small quantity of oil on trituration with methyl alcohol yielded some 2-hydroxy-4-methoxyphenyl benzyl ketone (m. p. and mixed m. p. 90°), but no coumarin was detected. Acidification of the alkaline washings yielded only a minute quantity of oily matter.

7-Methoxy-3′ : 4′-methylenedioxy-2-styryl-3-phenylchromone.—A solution of the above chromone (0·5 g.) and piperonal (0·3 g.) in alcohol (30 c.c.) containing sodium (0·05 g.) was kept for 3 days at room temperature. The *styryl* derivative which separated crystallised from alcohol in pale yellow needles (0·3 g.), m. p. 246° (Found : C, 75·8; H, 4·4. $C_{25}H_{18}O_5$ requires C, 75·8; H, 4·5%).

Action of Sodium Propionate and Propionic Anhydride on 2-Hydroxy-4-methoxyphenyl Benzyl Ketone.—The ketone (10 g.), sodium propionate (20 g.), and propionic anhydride (30 g.) were heated together under reflux for 8 hours at 190°. The product was poured into water and distilled with steam. The pale brown, crystalline residue was recrystallised from absolute alcohol, giving *7-methoxy-3-phenyl-2-ethylchromone* (8 g.) in long colourless needles, m. p. 119·5° (Found : C, 76·9; H, 5·6. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7%). The alcoholic mother-liquor was kept over-night with a solution of sodium ethoxide (2 g. of sodium), the total volume being approximately 100 c.c. The solution was diluted with water and treated as described previously. No coumarin was detected, the only products isolated being a further quantity of the ethylchromone and some 2-hydroxy-4-methoxyphenyl benzyl ketone.

Action of Sodium Propionate and Propionic Anhydride on 2-Hydroxy-4-methoxyacetophenone.—A mixture of 2-hydroxy-4-methoxyacetophenone (40 g.), sodium propionate (100 g.), and propionic anhydride (150 g.) was heated in an oil-bath at 200° for 48 hours. The mixture was poured into water, and propionic acid removed with steam. From the solid residue, by treatment with ether, 7-methoxy-3 : 4-dimethylcoumarin (10 g.) was obtained, which crystallised from alcohol in long needles, m. p. 142° (Found : C, 70·6; H, 5·95. Calc. for $C_{12}H_{12}O_3$: C, 70·6; H, 5·9%). The ethereal solution was repeatedly washed with aqueous alkali to remove unchanged hydroxy-ketone (8 g.). Evaporation of the ether, followed by distillation of the residue at 3 mm., yielded a yellow oil (28 g.), which gradually solidified and after crystallisation from alcohol gave a further quantity of the coumarin (8 g.). The alcoholic mother-liquor,

after standing over-night in the presence of alcoholic sodium ethoxide (10 g. of sodium; total volume of solution, 250 c.c.), was diluted with water, and the separated oil extracted with ether. After removal of solvent from the dried extract, the residue was agitated with light petroleum, and the separated solid (2·5 g.) crystallised from alcohol, 7-methoxy-2-ethylchromone being obtained in colourless needles, m. p. 82° (Found: C, 70·5; H, 5·9. Calc. for $C_{12}H_{12}O_3$: C, 70·6; H, 5·9%), not depressed by the authentic chromone prepared by the method of Heilbron, Hey, and Lowe (*loc. cit.*).

Acidification of the aqueous alkaline solution with acetic acid liberated an oil, which was extracted with ether. The ethereal solution was washed first with aq ueons sodium carbonate, which removed 2-hydroxy-4-methoxybenzoic acid (1·5 g., m. p. and mixed m. p. 157°), and then with aqueous sodium hydroxide, which extracted 5-methoxy-2-propionoacetylphenol (3·6 g., m. p. and mixed m. p. 83·5°) (Found: C, 64·9; H, 6·2. Calc. for $C_{12}H_{14}O_4$: C, 64·8; H, 6·3%). Evaporation of the ether gave a further quantity of 7-methoxy-3 : 4-dimethylcoumarin (9·9 g.).

An alternative method of treating the product after the initial separation of coumarin consisted in the repeated extraction of the distillate (47 g.) with a mixture of equal parts of concentrated hydrochloric acid and water. Neutralisation of the acid extract deposited 7-methoxy-2-ethylchromone (13·4 g.), which separated from ether–light petrolenm in cubes, m. p. 82°. The residue from the extraction gave 7-methoxy-3 : 4-dimethylcoumarin (19·5 g.), which separated from aqneous alcohol in colourless needles, m. p. 142°.

5-*Methoxy-2-propionoacetylphenol*.—This was prepared by the method of Heilbron, Hey, and Lowe (*loc. cit.*). The precipitated diketone was boiled in alcoholic solution with charcoal, and after filtration 5-methoxy-2-propionoacetylphenol separated in colourless needles, m. p. 83·5°.

A portion of the diketone (0·5 g.) was boiled for 5 minutes with glacial acetic acid (5 c.c.) and a few drops of concentrated hydrochloric acid. The solution was poured into water and extracted with ether, and the extract washed with aqueous sodinm carbonate. Evaporation of the ether gave 7-methoxy-2-ethylchromone, which was recrystallised from ether–light petroleum (m. p. and mixed m. p. 82°). A second portion of the diketone (1 g.) was boiled nnder refinx for ½ hour with 10% aqueous sodium hydroxide (60 c.c.). The cold solution was acidified and extracted with ether, and the extract washed first with aqueons sodium carbouate and then with aqueous sodium hydroxide. Acidification of the carbonate washings liberated 2-hydroxy-4-methoxybenzoic acid, which separated in needles from dilute acetic acid (0·5 g., m. p. and mixed m. p. 157°). The sodium hydroxide washings were acidified and extracted with ether, evaporation of which gave 2-hydroxy-4-methoxyacetophenone, which separated from aqueous alcohol in needles (m. p. and mixed m. p. 48°).

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65. *Derivatives of* tert.-*Butylbenzene and Transmitted Polar Effects.*

By (the late) JOHN B. SHOESMITH and ALEXANDER MACKIE.

IN continuation of the previous investigation (J., 1928, 2334) m- and p-tert.-*butylbenzyl bromides* have been prepared and the lability of the halogen in them investigated. Many fruitless attempts were made to obtain *o-tert.*-butylbenzyl bromide.

The isomeric *tert.*-butylbenzoic acids were also prepared in order to trace any regularities which might appear in their dissociation constants, since tbis is one of the properties influenced by substituent groups.

The main conclusion which has emerged is that the introduction of the *tert.*-butyl group into a benzene nucleus produces a marked difference in the reactivity of groups attached to the *m*- and *p*-positions.

The Reduction of m- *and* p-tert.-*Butylbenzyl Bromides*.—With hydriodic acid, the rate of reduction was $m > p$, which shows that the electromeric effect of the *p-tert.*-butyl group diminishes the reactivity of the bromine atom.

The *tert.*-butyl group is electron-repelling and therefore produces an inductive effect, whose sign is taken as negative (compare Robinson, J., 1932, 1445, footnote). This $-I$

effect should cause the greatest electronic pressure to be exerted at C_a, giving rise to the electromeric changes (I).

(I.)

(II.)

This inductive effect does not explain, however, the fact that the *tert.*-butylbenzyl bromides are more easily reduced than the unsubstituted benzyl bromide. It would appear, therefore, that there is a factor at work, other than the electromeric and inductive effects, which causes an increased " positivity " of the bromine atom in the butyl derivatives.

The Hydrolysis of m- *and* p-tert.-*Butylbenzyl Bromides.*—The electromeric effect due to the *tert.*-butyl group is again apparent in the more rapid hydrolysis in aqueous alcohol of *p-tert.*-butylbenzyl bromide than of the *m*-compound, a reversal of the order of reactivity which was observed in hydriodic acid.

The rate of hydrolysis, $p > m >$ unsubstituted, indicates that there is an appreciable transmission of an influence to the *m*-position, and that at this point the effect is definitely opposite to that excited in the *p*-position. The inductive effect results in the two isomerides being more rapidly hydrolysed than the unsubstituted compound.

The Dissociation Constants of the tert.-*Butylbenzoic Acids.*—The *tert.*-butyl group produces, like the methyl group, an influence on the dissociation constant of the opposite sign from its general polar effect. This is illustrated by the fact that *o-tert.*-butylbenzoic acid ($K_o^{25^\circ} = 3{\cdot}5 \times 10^{-4}$) is stronger than benzoic acid ($K_u^{25^\circ} = 6{\cdot}5 \times 10^{-5}$) and *m-tert.*-butylbenzoic acid ($K_m^{25^\circ} = 5{\cdot}2 \times 10^{-5}$) is weaker (compare Bennett and Mosses on the corresponding toluic acids; J., 1930, 2366). The abnormally high dissociation constant of *o-tert.*-butylbenzoic acid is probably due to a direct polar effect of the substituent on the carboxyl group (Lapworth and Manske, J., 1928, 2539). A comparison of the *m*- and *p*-derivatives, however, shows that the presence of the electromeric effect is also to be recognised here, since the *p*-compound (II) is the weaker acid.

Experimental.

m-tert.-*Butylbenzyl Bromide.*—The requisite quantity of bromine was volatilised in a current of dry air and passed into *m-tert.*-butyltoluene at its b. p. The butylbenzyl bromide formed was boiled with formic acid (100%) for 25 minutes to remove di- or tri-bromo-derivative and when cold the bromide was separated, washed in turn with water and sodium carbonate solution, and extracted with ether. The ethereal layer was shaken with sodium bisulphite solution to remove aldehyde, the solvent evaporated, the bromide dissolved in benzene, and the solution saturated with dry hydrogen bromide to convert any benzyl alcohol into bromide. After removal of the benzene, the bromide was fractionated in a vacuum (modification of the Widmer flask; *Helv. Chim. Acta*, 1924, **7**, 52). The portion, b. p. 124—126°/13 mm., had a low percentage of hydrolysable bromine, probably owing to the difficulty of converting the last trace of alcohol (formed during purification) back into the bromide. The impure butylbenzyl bromide was therefore gently heated with a slight excess of phosphorus pentabromide, the mixture kept over-night, the excess of phosphorus pentabromide removed, and the product fractionated in a vacuum, m-tert.-*butylbenzyl bromide* being obtained as a colourless non-lachrymatory liquid, b. p. 115·5°/8 mm. (Found : Br, 35·0. $C_{11}H_{15}Br$ requires Br, 35·25%).

p-tert.-*Butylbenzyl Bromide.*—A weighed quantity of bromine was slowly added to *p-tert.*-butyltoluene (b. p. 190—193°; Verley, *Bull. Soc. chim.*, 1898, **19**, 67) at 115°. The butylbenzyl bromide was purified in a manner similar to that by which the *m*-isomeride was obtained pure. The portion, b. p. 132·5—134·5°/15 mm., was cooled to − 16° and the solid obtained was crystallised from absolute alcohol at − 18°. p-tert.-*Butylbenzyl bromide* is a colourless liquid at the ordinary temperature, b. p. 132·5°/14 mm., with slight lachrymatory properties. It is hygroscopic and darkens on keeping. The solid crystallises from absolute alcohol and light petroleum at − 18° in colourless prismatic needles, m. p. 12—13° (Found : Br, 35·3%). Verley (*loc. cit.*) does not describe this compound fully and states that it cannot be distilled without decomposing. He did not obtain it crystalline.

m-tert.-*Butylbenzoic Acid.*—*m-tert.*-Butylbenzyl bromide was oxidised by potassium permanganate; the acid obtained crystallised from water in white plates, m. p. 127°. The same

acid was prepared by the action of carbon dioxide on the Grignard compound formed from magnesium and *m*-bromo-*tert.*-butylbenzene. The latter method of preparation appeared necessary in order to prove the constitution of the acid obtained in the former case, since some doubt exists in the literature as to the constitution of this acid obtained by oxidation methods (compare Kelbe,* *Ber.*, 1883, **16**, 620; Effront,* *Ber.*, 1884, **17**, 2330).

p-tert.-*Butylbenzoic Acid.*—*p-tert.*-Butyltoluene or *p-tert.*-butylbenzyl bromide was heated with nitric acid (*d* 1·20) for 6 hours, *p-tert.*-butylbenzoic acid being obtained. It crystallised from alcohol in rhombic prisms (compare Bialobrzeski, *Ber.*, 1897, **30**, 1775), m. p. 165° (Verley, *loc. cit.*, p. 71, gives 164°).

Reduction of m- *and* p-tert.-*Butylbenzyl Bromides.*—10 C.c. of a standard solution of the bromide and 10 c.c. of constant-boiling hydriodic acid were placed in a graduated flask and made up to 25 c.c. with glacial acetic acid, and the contents mixed. The flask was then placed in a thermostat at 110°, and the amount of bromide reduced in a definite time estimated. The results are in Table I, where *t* is the time in hours and *x* the percentage changed.

TABLE I.

t	1½	3	6
m-Isomeride, *x*	58	79	97
p-Isomeride, *x*	48	70	93

The order of reduction was unchanged at 25° and 100°.

Reduction of benzyl bromide at 110°: $x = 34$, 55, and 78 for $t = 1\frac{1}{2}$, 3, and 6 respectively (Shoesmith, Hetherington, and Slater, J., 1924, **125**, 1316).

Isolation and Identification of the Reduction Product from p-tert.-*Butylbenzyl Bromide.*—The bromide (1·5 g.) was dissolved, in a stoppered cylinder, in 15 c.c. of a solution of hydrogen iodide in glacial acetic acid. The cylinder was placed in a thermostat at 25° for 10 days, and the product then poured into water. The solid which separated was recrystallised from dilute acetic acid, forming colourless plates, m. p. 29·5—30·5°, undepressed by p-tert.-*butylbenzyl iodide* prepared by heating the bromide under reflux in acetone solution with potassium iodide for several hours (Found: I, 46·0. $C_{11}H_{15}I$ requires I, 46·3%).

Hydrolysis of m- *and* p-tert.-*Butylbenzyl Bromides.*—A satisfactory velocity constant could not be obtained at 60°, owing to the rapidity of hydrolysis. The hydrolysis was therefore carried out at 25°. Approximately 0·5 g. of the bromide was weighed into a 100 c.c. graduated flask and 90 c.c. of absolute alcohol, followed by 10 c.c. of water, were added; the contents were well mixed and then made up to 100 c.c. with absolute alcohol. 10 C.c. were withdrawn at stated intervals, and the hydrobromic acid estimated. A satisfactory unimolecular velocity constant (*k*) was obtained in each case, the time being measured in hours.

TABLE II.

Compound.	$k \times 10^6$.	Mean $k \times 10^6$.
Benzyl bromide		125 †
m-tert.-Butylbenzyl bromide	190, 192, 193	192
p-tert.-Butylbenzyl bromide	334, 336, 329	333

† Shoesmith and Rubli, J., 1927, 3099.

Dissociation Constants of the Isomeric tert.-*Butylbenzoic Acids.*—These were estimated by the usual Kohlrausch conductivity method at 25°. Satisfactory results could only be obtained when the cell electrodes were small and almost 1 cm. apart. Owing to the sparing solubility of the *m*- and *p*-isomerides, saturated solutions of which had concentrations of approximately *N*/2000 and *N*/3500 respectively, and the unreliability of observations at dilutions greater than these, the dissociation constants were found at one dilution only for all three acids, namely, approximately *N*/3500. The molecular conductivity at this dilution was then calculated from the usual formula. The most satisfactory method of obtaining the conductivity at infinite dilution, μ_∞, was by application of the rule, formulated by Ostwald, that the molecular conductivity at infinite dilution is the same for acids with the same number of atoms in the molecule. The *tert.*-butylbenzoic acids have 27 atoms in their molecule, from which $\mu_\infty^{25°} = 368$ (Ostwald Luther, "Physiko-Chemische Messungen," Leipzig, 1910, p. 482).

* References which describe compounds as containing *iso*butyl when in reality they contain *tert.*-butyl are marked with an asterisk (compare Shoesmith and Mackie, *loc. cit.*).

TABLE III.

Compound.	Dissociation constant.
Benzoic acid	$6{\cdot}5 \times 10^{-5}$
o-tert.-Butylbenzoic acid †	$3{\cdot}5 \times 10^{-4}$
m-tert.-Butylbenzoic acid	$5{\cdot}2 \times 10^{-5}$
p-tert.-Butylbenzoic acid	$4{\cdot}2 \times 10^{-5}$

† J., 1928, 2339.

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EDINBURGH UNIVERSITY. [*Received, December 10th,* 1935.]

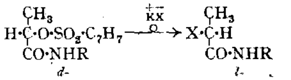
66. *Walden Inversion Reactions of* d-(+)α-p-*Toluenesulphonoxypropionic Acid and Amide and their Derivatives.*

By C. M. BEAN, J. KENYON, and H. PHILLIPS.

THE substitution reactions of acids are frequently complicated by the carboxyl group: Holmberg, for example (*J. pr. Chem.*, 1913, **87**, 456), showed that the sign of rotation of the malic acid obtained on hydrolysis of bromosuccinic acid depends on the experimental conditions employed, and demonstrated that malolactone is an intermediate product in the reaction. Intermediate lactone formation may also explain (Kenyon and Phillips, *Trans. Faraday Soc.*, 1930, **26**, 451) the difference in configuration of the products obtained from amino-acids and their esters under the action of either nitrous acid or nitrosyl bromide.

In such substitution reactions, the ionised carboxyl group can be considered to displace and react as though it were the entering anion. Additional evidence on the influence of carboxyl and related groups on the course of substitution reactions, and on the stereochemical factors that tend to augment or diminish this influence, has now been obtained by a study of the reactions of * *d*-(+)α-*p*-toluenesulphonoxypropionic acid, its amide, and some of its substituted amides. This series of compounds was chosen for investigation because it has been shown that the *p*-toluenesulphonoxy-group of the ethyl ester of the acid can be replaced by anions with inversion (Kenyon, Phillips, and Turley, J., 1925, **127**, 399), and also because the carboxyl and related groups in these compounds are conveniently situated for displacing the α-*p*-toluenesulphonoxy-group intramolecularly, when the experimental conditions are favourable.

As indicated below, the replacement of the α-*p*-toluenesulphonoxy-groups in the neutral compounds of this series—amide and anilide—by either the acetoxy- or the benzoyloxy-group was proved to occur with inversion.



R = H; C_6H_5. X = $O{\cdot}CO{\cdot}CH_3$; $O{\cdot}CO{\cdot}C_6H_5$.

This was accomplished by preparing the *d*-α-acetoxy- and -benzoyloxy-derivatives from either *d*-(−)lactic acid or a derivative of this acid by the following reactions, which are unlikely to lead to configurative change: *d*-(+)α-acetoxypropionamide, *d*-(−)lactic acid ⟶ *d*-(+)α-acetoxypropionic acid ⟶ *d*-(+)α-acetoxypropionyl chloride ⟶ *d*-(+)α-acetoxypropionamide; *d*-(−)α-benzoyloxypropionamide, ethyl *d*-(+)lactate ⟶ *d*-(+)α-hydroxypropionamide ⟶ *d*-(−)α-benzoyloxypropionamide; *d*-(+)α-acetoxypropionanilide from *d*-(+)α-acetoxypropionyl chloride; *d*-(−)α-benzoyloxypropionanilide from *d*-(−)α-benzoyloxypropionylchloride. Attempts to prepare *d*-α-acetoxy- or -benzoyl-

* The signs (+) and (−) are used in place of the terms dextrorotatory and lævorotatory; the letters *d*- and *l*- denote configurations. It is assumed that (−) lactic acid has a *d*-configuration and, in the theoretical portion of the paper, that all the experiments were made on *d*-compounds.

oxy-propion-β-naphthalide by reactions unlikely to lead to configurative change were unsuccessful. As in some of the reactions of ethyl *d*-(+)α-*p*-toluenesulphonoxypropionate (Kenyon, Phillips, and Turley, *loc. cit.*), many of the above replacement reactions occurred with little racemisation: α-acetoxypropionamide, for example, being obtained from ethyl *d*-(+)lactate, α_{5461} + 10·66° (*l*, 1), and from *d*-(+)α-*p*-toluenesulphonoxypropionamide (prepared from a sample of this ester) with α_{5461} + 17·8° and α_{5461} − 16·9° (*l*, 1) respectively.

d-(+)α-*p*-Toluenesulphonoxypropionic acid does not undergo similar reactions with either potassium acetate, benzoate or thiocyanate, because its salts readily hydrolyse into *l*-(−)lactic acid and *p*-toluenesulphonic acid. With lithium chloride in acetone or aqueous acetone, *d*-(+)α-*p*-toluenesulphonoxypropionic acid reacted smoothly to give α-chloropropionic acid. The rotations of the α-chloro-acids obtained under the various experimental conditions employed are in Table I.

TABLE I.

Rotatory power of *p*-toluenesulphonoxypropionic acid used. $[\alpha]_{5461}$ in methyl alcohol (*c*, 5).*	Form in which the sulphonate was present.	Reaction medium.	Proportion of lithium chloride, mols.	Rotatory power of α-chloropropionic acid † produced, α_{5461} (*l*, 1).	Result.
+ 57·0°	Acid	Dry acetone (40 c.c.), 1 c.c. water	1·2	− 15·82°	Inversion
− 24·3	,,	Moist acetone (50 c.c.)	1·2	+ 7·55	,,
− 24·3	,,	Acetone–water (20 c.c., 1 : 1)	3·0	+ 7·45	,,
+ 25·0	,,	Water (20 c.c.)	1·2	− 4·31	,,
+ 25·0	,,	*N*/10-HCl (20 c.c.)	1·2	− 4·65	,,
+ 25·0	K salt	Moist acetone (20 c.c.)	1·2	+ 9·55	No inversion
+ 57·0	,,	Moist acetone (20 c.c.)	1·2	+ 16·78	,,
+ 25·0	NH_4 salt	Moist acetone (20 c.c.)	1·2	+ 7·12	,,
− 20·1	Ba salt	Moist acetone (40 c.c.)	1·2	− 6·19	,,
+ 25·0	Aniline salt	Moist acetone	1·2	+ 4·43	,,

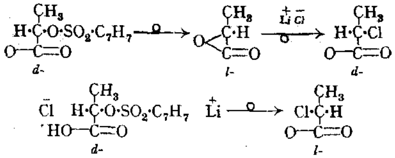
* For the optically pure acid, $[\alpha]^{25°}_{5461}$ 57·8° (Kenyon, Phillips, and Turley, *loc. cit.*).

† Only two rotations for α-chloropropionic acid in the homogeneous state appear to be recorded in the literature: α_{5893} − 2·36° (*l*, 1) (Frankland and Garner, J., 1914, **105**, 1101; acid obtained by the hydrolysis of α-chloropropionyl chloride); α_{5893} + 2·15° (*l*, 1) [Levene and Haller, *J. Biol. Chem.*, 1929, ., 707; acid obtained by the oxidation of (−)αγ-dimethylallyl chloride].

From the experiments of Kenyon, Phillips, and Turley (*loc. cit.*), and subsequent unpublished work, it can be concluded that ethyl (+)α-chloropropionate has the same configuration as ethyl (+)lactate. Since (+)α-chloropropionic acid gives ethyl (+)α-chloropropionate on esterification, it must be configuratively similar to ethyl (+)lactate. Hence *d*-(+)α-*p*-toluenesulphonoxypropionic acid obtained by the hydrolysis of ethyl (+)α-*p*-toluenesulphonoxypropionate [prepared from ethyl *d*-(+)lactate by methods unlikely to lead to configurative change; Kenyon, Phillips, and Turley, *loc. cit.*] has the same configuration as (+)α-chloropropionic acid. It is thus possible to determine, as recorded in Table I, which of the α-chloropropionic acids were produced with inversion. The conclusion reached is that the *d*-(+)α-*p*-toluenesulphonoxypropionic acid reacts with lithium chloride with inversion, but its salts give configuratively similar acids.

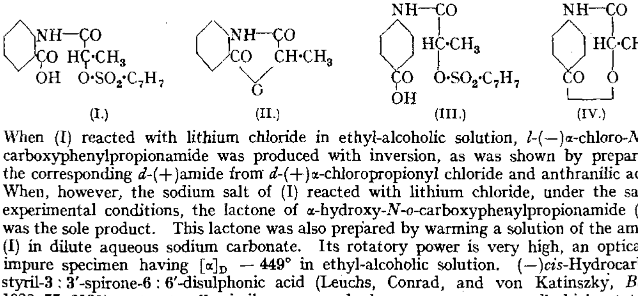
Although the salts of *d*-(+)α-*p*-toluenesulphonoxypropionic acid yield *d*-(+)α-chloropropionic acids, it is probable that inversion reactions occur during their formation. As indicated in the scheme on p. 305, the ionised carboxyl groups of these salts compete successfully with the chlorine anions, and give rise to a lactone with inversion of configuration. This lactone in turn reacts with lithium chloride with inversion so that the resulting α-chloropropionic acid is the product of two consecutive inversion reactions and is therefore configuratively similar to the original salt. On the other hand, the non-ionised carboxyl group of the acid does not compete with the entering chlorine anions, which react in the

usual manner with the *d*-acid and replace the α-*p*-toluenesulphonoxy-group with inversion. A further example of a double inversion reaction, probably involving the intermediate



formation of the lactone, is afforded by the interaction of the ammonium salt of the *d*-acid with potassium acetate. This gave *d*-(+)α-acetoxypropionic acid in marked contrast to the *l*-(−)α-acetoxy-derivatives obtained from the neutral *d*-(+)α-*p*-toluenesulphonoxypropionamides. Attempts to establish the formation of lactone by replacement of the *p*-toluenesulphonoxy-group of the ammonium salt of the acid in two stages, (*a*) eliminating ammonium *p*-toluenesulphonate by heating a dry chloroform solution of the salt, (*b*) treating the filtered chloroform solution supposed to contain the lactone with lithium chloride, did not give a conclusive result, since the amount of ammonium *p*-toluenesulphonate isolated was never equal to the calculated amount possible and the quantity of α-chloropropionic acid produced was always very small.

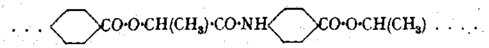
More conclusive evidence of the interference by carboxyl groups in substitution reactions was obtained, however, by a study of the reactions of *d*-(+)α-*p*-toluenesulphonoxy-*N*-*o*-carboxyphenylpropionamide (I) and also those of its *p*-isomeride (III).



(I.) (II.) (III.) (IV.)

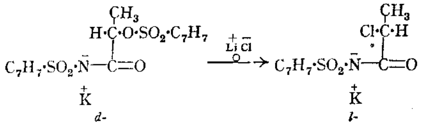
When (I) reacted with lithium chloride in ethyl-alcoholic solution, *l*-(−)α-chloro-*N*-*o*-carboxyphenylpropionamide was produced with inversion, as was shown by preparing the corresponding *d*-(+)amide from *d*-(+)α-chloropropionyl chloride and anthranilic acid. When, however, the sodium salt of (I) reacted with lithium chloride, under the same experimental conditions, the lactone of α-hydroxy-*N*-*o*-carboxyphenylpropionamide (II) was the sole product. This lactone was also prepared by warming a solution of the amide (I) in dilute aqueous sodium carbonate. Its rotatory power is very high, an optically impure specimen having $[\alpha]_D$ − 449° in ethyl-alcoholic solution. (−)*cis*-Hydrocarbostyril-3 : 3′-spirone-6 : 6′-disulphonic acid (Leuchs, Conrad, and von Katinszky, *Ber.*, 1922, **55**, 2131), a structurally similar compound, also possesses an unusually high rotatory power.

Like the *d*-(+)*o*-amide (I), the *p*-amide (III) and also its aniline salt reacted with lithium chloride in ethyl-alcoholic solution, *l*-(−)α-chloro-*N*-*p*-carboxyphenylpropionamide being produced with inversion. All attempts, however, to obtain this chloro-amide by the interaction of the sodium salt of (III) with lithium chloride failed. The only definite product isolated was a sulphur-free, white, amorphous substance, which gave analytical data in agreement with (IV). This substance was obtained also by heating an aqueous solution of the sodium salt of the amide (III) at 100° for some hours. In view of its insolubility in common solvents and its amorphous character, it appears probable that this substance is a linear condensation product.



Its formation is possibly the result of end-on association, favoured by the presence of

dipoles and followed by intermolecular inversion reactions, and illustrates how the course of a reaction can be determined by the molecular configuration of the reacting molecules. This reaction can be contrasted with the reaction of the o-isomeride (I), in which the molecular configuration favours lactone formation by intramolecular reaction. The reactions of *d*-(+)α-*p*-toluenesulphonoxy-*N*-*p*-toluenesulphonylpropionamide (V) and its sodium salt provide examples of the influence of the size of a potential entering anion on the course of a reaction.

(V.)  (VI.)

Although the salts of this compound contain an ionised acidic group conveniently situated to favour intramolecular reaction, such reactions do not occur, probably because the *p*-toluenesulphonylimide group is too large to approach close enough to the α-carbon atom to enable it to replace the α-*p*-toluenesulphonoxy-group. Thus the *d*-*p*-toluenesulphonylamide and its potassium and lithium salts reacted with lithium chloride in alcoholic solution to give *l*-(—)α-chloro-*N*-*p*-toluenesulphonylpropionamide (VI) with inversion, as was proved by preparing the corresponding *d*-(+)amide by the interaction of *d*-(+)α-chloropropionyl chloride with sodium *p*-toluenesulphonamide.

As a possible example of the course of a reaction being determined by the molecular configuration of an external entering anion, the reaction between the salts of *p*-toluenesulphinic acid and alkyl halides can be quoted. Such reactions do not give rise to sulphinic esters, as might be expected, but to sulphones. The reason for this may be that the sulphur atom of the *p*-toluenesulphinate anion, being situated at the apex of a tetrahedron (Phillips, J., 1925, **127**, 2252), can approach more nearly to the carbon atom at the centre of the tetrahedron of which the halogen atom occupies the apex than can either of the anionic oxygen atoms.

When heated in ethyl-alcoholic solution, the potassium salt of (V) gave *d*-(+)α-ethoxy-*N*-*p*-toluenesulphonylpropionamide, the configuration of which was proved by preparing it from ethyl *d*-(+)α-ethoxypropionate. This reaction of the *p*-toluenesulphonylpropionamide is a further example of the tendency of sulphonic esters to undergo fission at the O–S linkage in the presence of alcohols and to give rise to ethyl *p*-toluenesulphonate, which ethylates the hydroxy-compound simultaneously produced (Phillips, J., 1923, **123**, 44).

EXPERIMENTAL.

Partial Resolution of α-p-*Toluenesulphonoxypropionic Acid.*—To an ice-cold solution of *dl*-α-*p*-toluenesulphonoxypropionic acid (15 g.) and quinine (20 g.) in acetone (25 c.c.), ethyl acetate (75 c.c.) was added, and the mixture cooled in ice. The quinine salt (18 g.) obtained proved too unstable to be recrystallised; when decomposed with dilute sulphuric acid, it gave (+)α-*p*-toluenesulphonoxypropionic acid, $[\alpha]_{5461}$ + 27·2° (*l*, 2; *c*, 5·00) in methyl alcohol. The filtrate, after decomposition, yielded the (—)acid with approximately the same rotatory power. The rotatory power of the *d* + *dl*-acid increases slowly when it is recrystallised from benzene and light petroleum, but the optically pure acid is more readily obtained from *d*-lactic acid by Kenyon, Phillips, and Turley's method (*loc. cit.*).

d-(+)α-p-*Toluenesulphonoxypropionyl Chloride.*—*d*-(+)α-*p*-Toluenesulphonoxypropionic acid (15 g., $[\alpha]_{5461}$ + 48·5° in methyl alcohol) and thionyl chloride (20 c.c.) were heated together for 3 hours, and the excess of reagent removed at 100° under diminished pressure. The residual d-(+)α-p-*toluenesulphonoxypropionyl chloride*, b. p. 140—145° < 0·1 mm., set to a mass of phenol-like crystals (13·5 g.), m. p. 53°, with $[\alpha]_{5461}$ + 3·69° (*l*, 2; *c*, 4·607) in benzene solution (For complete hydrolysis, 0·3082 g. required 0·1400 g. of sodium hydroxide. Calc., 0·1411 g.).

d-(+)α-*Chloropropionyl Chloride from* l-(—)α-p-*Toluenesulphonoxypropionyl Chloride.*—*l*-(—)α-*p*-Toluenesulphonoxypropionyl chloride (10 g., $[\alpha]_{5461}$ — 42·4°, supercooled, from (—)acid, $[\alpha]_{5461}$ — 24·3° in methyl alcohol) and lithium chloride (3 g., 1·6 mols.) in dry acetone (30 c.c.)

were heated under reflux for 5 hours. The (+)α-chloropropionyl chloride produced was converted into ethyl (+)α-chloropropionate by the addition of ethyl alcohol (5 c.c.) and a little potassium carbonate. When isolated in the usual manner, it (0·75 g.) had b. p. 135—137°, $\alpha_{5461}^{18°}$ + 1·17° (*l*, 0·25).

d-(+)α-*Acetoxypropionamide from* l-(−)α-p-*Toluenesulphonoxypropionamide*.—A solution of *l*-(−)α-*p*-toluenesulphonoxypropionamide (10 g., $[\alpha]_{5461}$ − 37·8° in ethyl alcohol *) and fused potassium acetate (4·5 g.) in ethyl alcohol (25 c.c.) was heated under reflux for 1·5 hours and then evaporated to dryness. The residue was mixed with acetone, and the filtered solution dried with sodium sulphate. The resulting d-(+)α-*acetoxypropionamide* (3 g.), after three distillations, b. p. 128—131° < 0·1 mm., had constancy of rotatory power, $\alpha_{5461}^{18°}$ + 4·26° (*l*, 0·25), $n_D^{20°}$ 1·4565 (supercooled), m. p. 59—60° (needles) (Found : N, 10·9. $C_5H_9O_3N$ requires N, 10·7%). It is very soluble in water but only sparingly in ether.

l-(−)α-*Acetoxypropionamide from Ethyl* l-(−)*Lactate*.—Ethyl *l*-(−)lactate † (20 g.; α_{5461} − 10·66°, *l* 1) was saponified witb sodium hydroxide (8 g.) in the minimum amount of water and the syrupy sodium *l*-lactate obtained on evaporation was mixed with a slight excess of cold hydrochloric acid. The product was mixed with acetone (50 c.c.) and *iso*propyl ether (50 c.c.) and sufficient sodium sulphate to remove the water. The dry *l*-lactic acid, after removal of the solvents, was mixed with acetyl chloride (25 g.), and the product fractionated under reduced pressure; the *l*-(−)α-acetoxypropionic acid (17 g.) had b. p. 135—136°/24 mm. and $\alpha_{5461}^{18°}$ − 47·8° (*l*, 1). This acid (17 g.), mixed with thionyl chloride, yielded *l*-α-acetoxypropionyl chloride (18 g.), b. p. 78°/22 mm. A portion (5 g.) in dry methylene chloride (30 c.c.) was treated with dry ammonia, a large excess being avoided. Filtration and evaporation yielded l-(−)α-*acetoxypropionamide* (3 g.), b. p. 104—105° < 0·1 mm., m. p. 59—60° alone and when mixed with the amide prepared as described above, α_{5461} − 17·7° (*l*, 1 in supercooled state) (Found : N, 10·7%).

l-(+)α-*Benzoyloxypropionamide from* d-(+)α-p-*Toluenesulphonoxypropionamide*.—*d*-(+)α-*p*-Toluenesulphonoxypropionamide (5 g., $[\alpha]_{5461}$ + 37·4° in ethyl alcohol) was heated at 100° for 4 hours with potassium benzoate (4 g.) and water (20 c.c.) : on cooling, d-(+)α-*benzoyloxypropionamide* (3·5 g.) separated in short needles, m. p. 118—125°. After crystallisation from methyl alcohol and *iso*propyl ether, it was obtained in tablets (1·7 g.), m. p. 127—128°, $[\alpha]_{5461}$ + 66·6°, $[\alpha]_{5790}$ + 56·8° (*l*, 2; *c*, 4·74) in ethyl alcohol (Found : N, 7·4. $C_{10}H_{11}O_3N$ requires N, 7·3%).

l-(+)α-*Benzoyloxypropionamide from Ethyl* l-(−)*Lactate*.—The lactate (15 g.; α_{5461} − 10·66°, *l* 1) was saturated with ammonia at 0° and left over-night at room temperature in a closed bottle. After removal of unchanged ester by distillation under diminished pressure, *l*-lactamide (6 g.), m. p. 72°, was obtained. This was mixed with pyridine (10 g.) and freshly distilled benzoyl chloride (10 g.) : after addition of dilute hydrochloric acid the l-(+)α-*benzoyloxypropionamide* was extracted with chloroform and crystallised from ethyl alcohol. It had m. p. 125—126°, and $[\alpha]_{5461}$ + 61·8°, $[\alpha]_{5790}$ + 53·7° (*l*, 2; *c*, 5·359) in ethyl alcohol (Found : N, 7·1%).

l-(−)α-p-*Toluenesulphonoxypropionanilide*.—Aniline (10 c.c.) was triturated with *l*-(−)α-*p*-toluenesulphonoxypropionyl chloride (3 g. from optically pure acid; Kenyon, Phillips, and Turley, *loc. cit.*) in dry ether. The anilide (4 g.) separated from aqueous ethyl alcohol in oblong plates, m. p. 132°, $[\alpha]_{5461}$ − 104·2°, $[\alpha]_{5790}$ − 91·5° (*l*, 2; *c*, 1·733) in ethyl alcohol.

d-(+)α-*Acetoxypropionanilide from* l-(−)α-p-*Toluenesulphonoxypropionanilide*.—The anilide (4 g., $[\alpha]_{5461}$ − 41° in ethyl alcohol) was heated with an alcoholic solution of potassium acetate (1·4 mols.) for 1 hour. d-(+)α-*Acetoxypropionanilide* was obtained by evaporation of the solvents and trituration of the dry residue with cold water. When either the proportion of potassium acetate or the period of heating was increased, lactanilide was produced. The crude acetate, m. p. 104°, $[\alpha]_{5461}$ + 5·37° (in ethyl alcohol), when crystallised (charcoal) from ethyl alcohol gave the optically inactive acetate, m. p. 124°; from the filtrate, the (+)acetate, $[\alpha]_{5461}$ + 12·7° in ethyl alcohol (*l*, 2; *c*, 2·200) was obtained (Found : N, 6·9. $C_{11}H_{13}O_3N$ requires N, 6·8%).

l-(−)α-*Acetoxypropionanilide* (Found : N, 6·9%), m. p. 121°, $[\alpha]_{5461}$ − 12·2° (*l*, 2; *c*, 1·026) in ethyl alcohol, was obtained as the more soluble fraction when the crude anilide ($[\alpha]_{5461}$ − 2·38°) from the interaction of aniline (7 c.c.) and (−)acetoxypropionyl chloride [3 g., from ethyl (−)lactate, α_{5461} − 6·76°, *l* 1] was recrystallised from ethyl alcohol.

* Kenyon, Phillips, and Turley (*loc. cit.*) give $[\alpha]_{5461}^{26°}$ + 40·4° for the optically pure *d*-amide in ethyl alcohol at the same concentration (*c*, 5).

† By calculation from data given by Wood, Such, and Scarf (J., 1923, **123**, 600), the rotation of optically pure ethyl lactate is $\alpha_{5893}^{18·5°}$ 11·65°, $\alpha_{5461}^{20°}$ 13·3° (*l*, 1).

d-(−)*α-Benzoyloxypropionanilide from* l-(+)α-p-*Toluenesulphonoxypropionanilide.*—The anilide (2·5 g., $[\alpha]_{5461}$ − 41° in ethyl alcohol), anhydrous potassium benzoate (1·5 g.), and absolute alcohol (20 c.c.) were heated under reflux for 3·5 hours. The *d*-(−)α-benzoyloxypropionanilide, isolated in the usual manner, had m. p. 160°, $[\alpha]_{5461}$ − 21·2°, and after recrystallisation from ethyl alcohol m. p. 160°, $[\alpha]_{5461}$ − 12·0°, (*l* 2; *c*, 0·7735) in ethyl alcohol.

l-(+)*α-Benzoyloxypropionanilide from Ethyl* l-(−)*Lactate.*—Dry *l*-lactic acid (20 g., from ethyl *l*-lactate, α_{5461} − 10·66°, *l* 1) was gently warmed with benzoyl chloride (25 g.) until the evolution of hydrogen chloride ceased, and the crude product was extracted with *iso*propyl ether. From the washed and dried extract, a mixture of α-benzoyloxypropionic and benzoic acids was isolated, which was warmed with thionyl chloride, the bulk of benzoyl chloride removed at 15 mm., and the residue distilled at low pressure. l-(+)*α-Benzoyloxypropionyl chloride* (5 g.) was obtained as a mobile liquid with a choking odour: b. p. 98° < 0·1 mm., $n_D^{20°}$ 1·5232, $[\alpha]_{5790}$ + 43·7°, $[\alpha]_{5461}$ + 51·3° (*l*, 1) (0·3190 g. required 0·1784 g. of sodium hydroxide for complete hydrolysis. Calc., 0·1806 g.). This chloride (2 g.) and aniline (3 g.) gave *l*-(+)α-benzoyloxypropionanilide, m. p. 160° (mixed with the anilide prepared from the sulphonate, m. p. 159—160°), $[\alpha]_{5461}$ + 15·0° (*l*, 2; *c*, 1·025) in ethyl alcohol.

l-(−)α-p-*Toluenesulphonoxypropiono*-β-*naphthalide.*—An ethereal solution of β-naphthylamine (in excess) was added to *l*-(−)α-*p*-toluenesulphonoxypropionyl chloride (2·8 g., from the optically pure acid; Kenyon, Phillips, and Turley, *loc. cit.*), and the solvent allowed to evaporate. After trituration with dilute hydrochloric acid the residue (6·1 g.) separated from ethyl alcohol in needles, m. p. 128° (Found: N, 3·6. $C_{20}H_{19}O_4NS$ requires N, 3·8%), $[\alpha]_{5780}$ − 108·5°, $[\alpha]_{5461}$ − 123·8° (*l*, 2; *c*, 1·023) in ethyl alcohol.

dl-α-p-*Toluenesulphonoxy*-N-p-*Toluenesulphonylpropionamide.*—*dl*-α-*p*-Toluenesulphonoxypropionyl chloride (35 g.) in ether (200 c.c.) was mixed with dry sodium *p*-toluenesulphonamide (150 g.; > 2 mols.). Heat was evolved, and after occasional shaking during 1 hour the ether was allowed to evaporate completely and the residue mixed with dilute hydrochloric acid; the dough-like insoluble product was washed with water and mixed with ice-cold potassium carbonate solution. *p*-Toluenesulphonamide was dissolved from the resulting crystalline precipitate by means of acetone (350 c.c.) and the insoluble potassio-α-*p*-toluenesulphonoxy-*N*-*p*-toluenesulphonylpropionamide with hydrochloric acid yielded dl-α-p-*toluenesulphonoxy*-N-p-*toluenesulphonylpropionamide*, which formed granular crystals, m. p. 137°, from benzene and light petroleum (Found: N, 3·65. $C_{17}H_{19}O_6NS_2$ requires N, 3·5%). Titration with 0·1*N*-sodium hydroxide and phenolphthalein gave equiv., 390. Calc., 396). An aqueous solution of the ammonium salt of this compound, mixed with potassium chloride solution, yielded the potassio-derivative as crystalline needles.

l-(−) α-p-*Toluenesulphonoxy*-N-p-*toluenesulphonylpropionamide.*—(−)α-*p*-Toluenesulphonoxypropionyl chloride {50 g., from (−)acid with $[\alpha]_{5461}$ − 34° in methyl alcohol}, was treated with sodium *p*-toluenesulphonamide as in the preceding experiment. The dough-like product obtained by the addition of hydrochloric acid was thoroughly washed with water, allowed to dry, and dissolved in chloroform (150 c.c.), in which *p*-toluenesulphonamide is but sparingly soluble. The syrup obtained after evaporation of the chloroform was dissolved in hot ethyl alcohol (360 c.c.) containing potassium carbonate (14 g.); *potassium* α-p-*toluenesulphonoxy*-N-p-*toluenesulphonylpropionamide* then crystallised. This was washed with a small amount of water to remove potassium carbonate, and the residue (57 g.) added to warm dry acetone (300 c.c.), in which the potassium salt of the *dl*-amide is almost insoluble. This (18 g.) was removed and the acetone filtrate was concentrated to 100 c.c., mixed with an equal volume of ethyl alcohol, and allowed to crystallise spontaneously. Long needles of the potassium salt of the *l*-amide (22 g.) were obtained, m. p. 160° (decomp.), and $[\alpha]_{5461}$ − 79·4° (*l*, 2; *c*, 1·306) in acetone (Found: N, 3·3. $C_{17}H_{18}O_6NS_2K$ requires N, 3·2%). On decomposition with dilute hydrochloric acid and extraction with methylene chloride the *l*-amide was obtained as a vitreous mass which would not crystallise.

l-(−)*α-Ethoxy*-N-p-*toluenesulphonylpropionamide from Potassium* l-α-p-*Toluenesulphonoxy*-N-p-*toluenesulphonylpropionamide.*—The *l*-potassium salt (5 g., $[\alpha]_{5893}$ −79·4° in acetone) in absolute alcohol (50 c.c.) was heated under reflux for 11 hours, the solvent removed, and the residue mixed with dilute hydrochloric acid. The resulting (−)*α-ethoxy*-N-p-*toluenesulphonylpropionamide* ($[\alpha]_D$ − 12·64°) separated from benzene and light petroleum in rectangular plates, m. p. 80—81°, $[\alpha]_{5893}$ − 10·0° (*l*, 2; *c*, 0·9985) in ethyl alcohol (Found: C, 53·9; H, 6·25; N, 5·2; equiv., 275. $C_{12}H_{17}O_4NS$ requires C, 53·2; H, 6·3; N, 5·2%; equiv., 271). The corresponding ethoxy-derivative prepared from optically inactive materials also had m. p. 80—81°.

l-(−)*α-Ethoxy*-N-p-*toluenesulphonylpropionamide from Ethyl* l-(−)*Lactate*.—Ethyl *l*-lactate (17 g.; $[\alpha]_{5893}$ − 8·7°, *l* 1), ethyl iodide (40 g.), and dry silver oxide (28 g.; 1·6 mols.) were heated together for 2 hours and the resulting ethyl *l*-α-ethoxypropionate (15 g.) was saponified with sodium hydroxide. The *l*-α-ethoxypropionic acid (12 g.), b. p. 104—105°/25 mm., obtained was warmed with thionyl chloride, and the *l*-α-ethoxypropionyl chloride redistilled twice, b. p. 40—49°/20 mm. This (5 g.) was dissolved in ether (30 c.c.) and mixed with sodium-*p*-toluenesulphonamide (12 g.). The *l*-(−)α-ethoxy-*N*-*p*-toluenesulphonylpropionamide (3 g.) thus prepared had m. p. 65—70°, $[\alpha]_{5893}$ − 21·4°. After crystallisation from benzene and light petroleum it had m. p. 79—80° (80—81° when mixed with the compound prepared by the action of ethyl alcohol on potassium *l*-α-*p*-toluenesulphonoxy-*p*-toluenesulphonylpropionamide) and $[\alpha]_{5893}$ − 21·0° (*l*, 2; *c*, 3·25) in ethyl alcohol.

d-(+)*α-Chloro*-N-p-*toluenesulphonylpropionamide from* l-(−)*α*-p-*Toluenesulphonoxy*-N-p-*toluenesulphonylpropionamide*.—Optically pure *l*-(−)α-*p*-toluenesulphonoxy-*N*-*p*-toluenesulphonylpropionamide (7 g.), lithium chloride (2 g.), and alcohol (50 c.c.) were heated under reflux for 3 hours. The resulting *d*-(+)α-chloro-*N*-*p*-toluenesulphonylpropionamide had m. p. 109° and $[\alpha]_{5461}$ + 17·7°: it separated from benzene and light petroleum in hairy crystals, m. p. 118°, $[\alpha]_{5461}$ + 29·7° (*l*, 2; *c*, 2·236) in ethyl alcohol. Further crystallisation did not alter appreciably either the m. p. or the rotatory power.

The lithium derivative of optically pure *l*-α-*p*-toluenesulphonoxy-*N*-*p*-toluenesulphonylpropionamide on similar treatment gave α-chloro-*N*-*p*-toluenesulphonylpropionamide having m. p. 118°, $[\alpha]_D$ + 23·2°, $[\alpha]_{5461}$ + 28·2° (*l*, 2; *c*, 4·1885) in ethyl alcohol.

d-(+)*α-Chloro*-N-p-*toluenesulphonylpropionamide from Ethyl* d-(+)*α-Chloropropionate*.—Ethyl *d*-(+)α-chloropropionate, b. p. 139—144°, α_{5893} + 7·68° (*l*, 1), prepared from ethyl *l*-lactate (50 g.; α_{5461} − 6·5°, *l* 1), pyridine (40 g.), and thionyl chloride (55 g.), was saponified with cold sodium hydroxide solution, and the resulting *d*-α-chloropropionic acid converted by means of thionyl chloride into *d*-α-chloropropionyl chloride * (24 g.), b. p. 110—120°, α_{5893} + 0·8°, which (15 g.) in ethereal solution with sodium *p*-toluenesulphonamide (2 mols.) gave *d*-(+)α-chloro-*N*-*p*-toluenesulphonylpropionamide (45 g.), m. p. 90—100°, $[\alpha]_{5461}$ + 6·5°. After crystallisation from benzene and light petroleum, it had $[\alpha]_{5461}$ + 13·7° (*l*, 2; *c*, 1·9275) in ethyl alcohol, m. p. 117—118°, either alone or mixed with any of the three specimens of this compound prepared as described above.

Ethyl l-(−)*Lactate from* l-(−)*α*-p-*Toluenesulphonoxypropionic Acid*.—l-(−)α-*p*-Toluenesulphonoxypropionic acid † (19 g., $[\alpha]_{5790}$ − 47·6° in methyl alcohol), fused potassium acetate (7·7 g.), and absolute alcohol (30 c.c.) were heated under reflux for 12 hours, the solvent removed, and the residue neutralised with sodium carbonate solution. The last traces of moisture having been removed, the mixture of salts was heated under reflux (8 hours) with ethyl *p*-toluenesulphonate (31·2 g.) and absolute alcohol (50 c.c.) to esterify the lactic acid produced. Dry ether (50 c.c.) was then added, the precipitated salts removed by filtration, the filtrate evaporated, and the ethyl lactate fractionally distilled, b. p. 46°/15 mm., until its rotatory power remained unchanged on redistillation. This reaction was carried out also in aqueous and in glacial acetic acid solutions, portions of the same specimen of (−)α-*p*-toluenesulphonoxypropionic acid being used; the rotatory powers (α_{5461}, *l* 1) of the three samples of ethyl *l*-lactate obtained were: from absolute alcohol, −10·07°; water, − 10·60°; glacial acetic acid, − 10·80°.

l-(−)*α-Acetoxypropionic Acid from* l-(−)*α*-p-*Toluenesulphonoxypropionate*.—*l*-(−)α-*p*-Toluenesulphonoxypropionic acid (10 g., $[\alpha]_{5893}$ − 34° in methyl alcohol) was dissolved in the calculated volume of a standardised solution of ammonia in dry acetone. The resulting solution was heated with potassium acetate (4·2 g.) for 45 minutes and an acetone solution of hydrogen chloride was then added in slight excess (Congo-red), followed by anhydrous sodium sulphate. When distilled, the dry acetone solution gave *l*-(−)α-acetoxypropionic acid (2 c.c.), b. p. 136—137°/16 mm., α_{5461} − 26·2° (*l*, 1) (Found: equiv., 132. Calc., 132).

d-(+)*α-Chloropropionic Acid from* l-(−)*α*-p-*Toluenesulphonoxypropionic Acid*.—*l*-α-*p*-Toluenesulphonoxypropionic acid (10 g., $[\alpha]_{5461}$ − 24·3° in methyl alcohol), lithium chloride (2 g.), and moist acetone (50 c.c.) were heated under reflux for 2 hours, the solvent removed, and ether (50 c.c.) and anhydrous sodium sulphate added. The α-chloropropionic acid (2 g.) obtained was distilled under reduced pressure, b. p. 88°/17 mm., and subsequently at atmospheric pressure (180—181°) until constancy of rotatory power was reached. The purity of the final

* This chloride has previously been isolated by Frankland and Garner (*loc. cit.*) with $\alpha^{18°}_{5893}$ + 0·2° (*l*, 1).

† Kenyon, Phillips, and Turley (*loc. cit.*) give $[\alpha]^{23°}_{5790}$ + 48·7° for the optically pure acid in methyl alcohol at the same concentration (*c*, 5).

product was verified by titration with alkali. This reaction was repeated in a number of other solvents: the results are in Table I.

In the experiment in which 0·1N-hydrochloric acid was used as the reaction solvent, the calculated quantity of calcium carbonate necessary to neutralise the hydrochloric acid was added before the chloro-acid was isolated by dilution of the reaction mixture with *iso*propyl ether and addition of sufficient anhydrous sodium sulphate to combine with any water present.

l-(−)*α-Chloropropionic Acid from Salts of* l-(−)α-p-*Toluenesulphonoxypropionic Acid and Lithium Chloride*.—These reactions were carried out in acetone solutions to which in the first place the sulphonate (10 g.) was added, followed by the calculated amount of the appropriate base. After the addition of lithium chloride (1·2 mols.) the solution was heated under reflux for about 2 hours. A very slight excess of concentrated hydrochloric acid, mixed with acetone, and then *iso*propyl ether and anhydrous sodium sulphate were added to the reaction mixtures and the α-chloropropionic acid produced was isolated by distillation, the purity of each specimen being checked by determination of its equivalent. The rotatory powers of the α-chloro-acids obtained are in Table I.

l-(−)α-p-*Toluenesulphonoxy*-N-o-*carboxyphenylpropionamide*.—*l*-α-*p*-Toluenesulphonoxypropionyl chloride {20 g., from (−)acid, $[\alpha]_{5461}$ − 40·2° in methyl alcohol} in dry ether (70 c.c.) was triturated with anthranilic acid (25 g.); the resulting l-α-p-*toluenesulphonoxy*-N-o-*carboxyphenylpropionamide* (30 g.) separated from benzene–light petroleum in oblong plates or rods, m. p. 131°, $[\alpha]_{5893}$ − 102·4° (*l*, 2; *c*, 1·660) in ethyl alcohol. Solutions of this (−)amide in organic solvents, notably benzene, showed a violet fluorescence. The *dl*-amide forms hexagonal plates, m. p. 150—151° (Found: equiv., 360. $C_{17}H_{17}O_6NS$ requires equiv., 363).

d-(+)*α-Chloro*-N-o-*carboxyphenylpropionamide from* l-(−)p-*Toluenesulphonoxy*-N-o-*carboxyphenylpropionamide*.—The (−)amide (5 g.), prepared as described above, lithium chloride (1 g.), and alcohol (50 c.c.) were heated under reflux for 8 hours; the resulting α-chloro-*N*-*o*-carboxyphenylpropionamide, m. p. 146—148°, had $[\alpha]_{5893}$ + 3·5° in ethyl alcohol and was completely soluble in dilute sodium carbonate solution. It separated from benzene and light petroleum in flat plates, m. p. 148°, $[\alpha]_{5893}$ + 3·34° (*l*, 2; *c*, 5·094) in chloroform.

Lactone of α-Hydroxy-N-o-*carboxyphenylpropionamide from the Sodium Salt of* l-α-p-*Toluenesulphonoxy*-N-o-*carboxyphenylpropionamide*.—The (−)amide (2·5 g.), prepared as described above, was neutralised in alcohol (20 c.c.) with sodium ethoxide, lithium chloride (1 g.) added, and the clear solution heated under reflux for 3·5 hours. No acidic substance could be isolated from the resulting, faintly alkaline solution; the chief product was a neutral compound (1·2 g.), which separated from alcohol in colourless needles, m. p. 236—238°, $[\alpha]_{5893}$ − 449° (*l*, 2; *c*, 0·9720) in ethyl alcohol. It was insoluble in sodium carbonate solution, but dissolved slowly in hot sodium hydroxide solution; it could be sublimed near its m. p. It was identified as the *lactone* of *α-hydroxy*-N-o-*carboxyphenylpropionamide* (Found: C, 62·9; H, 4·7. $C_{10}H_9O_3N$ requires C, 62·9; H, 4·7%). The lactone was prepared also by warming a solution of the amide in dilute aqueous sodium carbonate: optically active amide gave a (−)lactone, m. p. 237°, and the *dl*-amide a lactone, m. p. 186°.

d-(+)*α-Chloro*-N-o-*carboxyphenylpropionamide from* d-(+)*α-Chloropropionyl Chloride*.—A dry ethereal solution of *d*-α-chloropropionyl chloride (α_{5893} + 0·8°; *l*, 1; preparation, see p. 307) was triturated with an excess of anthranilic acid. The *d*-α-chloro-*N*-*o*-carboxyphenylpropionamide produced separated from benzene and light petroleum in plates, $[\alpha]_{5893}$ + 1·5° (*l*, 2; *c*, 4·1315) in chloroform, m. p. 147—148° [alone or when mixed with the (+)α-chloro-amide prepared as described above].

l-(+)*α*-p-*Toluenesulphonoxy*-N-p-*carboxyphenylpropionamide*.—*l*-α-*p*-Toluenesulphonoxypropionyl chloride {20 g., from (−)acid, $[\alpha]_{5893}$ − 29·9° in methyl alcohol} was converted into the *N*-*p*-carboxyphenylpropionamide by interaction with *p*-aminobenzoic acid. After crystallisation from acetic acid, the product (34 g.) had m. p. 166—167°, $[\alpha]_{5893}$ − 51·3° (*l*, 2; *c*, 4·7205) in ethyl alcohol. The corresponding *dl*-compound formed plates, m. p. 171° (Found: equiv., 66. $C_{17}H_{17}O_6NS$ requires equiv., 363).

d-(+)*α-Chloro*-N-p-*carboxyphenylpropionamide from* l-(−)α-p-*Toluenesulphonoxy*-N-p-*carboxyphenylpropionamide*.—The *l*-sulphonate (5 g.), prepared as described above, lithium chloride (1 g.), and absolute alcohol (50 c.c.) were heated under reflux for 2 hours. The resulting d-(+)α-chloro-*N*-*p*-carboxyphenylpropionamide (2·8 g.) separated from alcohol in rectangular plates, m. p. 230—231°, $[\alpha]_{5893}$ + 35·2° (*l*, 2; *c*, 3·325) in ethyl alcohol.

The "Lactone" of α-Hydroxy-N-p-*carboxyphenylpropionamide*.—Sodium *l*-(−)α-*p*-toluenesulphonoxy-*N*-*p*-carboxyphenylpropionamide {3 g.; prepared from *l*-(−)α-*p*-toluenesulphonoxypropionic acid with $[\alpha]_{5790}$ − 29·9° in methyl alcohol} in water (20 c.c.) was heated on the steam-

bath for 4 hours. The "*lactone*" (1 g.) (Found: C, 59·8; H, 4·8; N, 7·2. $C_{16}H_9O_3N$ requires C, 62·8; H, 4·7; N, 7·3%) separated in an extremely fine state of division and was filtered off with difficulty. It decomposed between 270° and 290° and was insoluble in all the common solvents except pyridine, in which it had $[\alpha]_{5893}$ − 161° (*l*, 2; *c*, 0·301).

d-(+)*α-Chloro*-N-p-*carboxyphenylpropionamide from the Aniline Salt of* l-(−)α-p-*Toluenesulphonoxy*-N-p-*carboxyphenylpropionamide*.—*l*-(−)α-*p*-Toluenesulphonoxy-*N*-p-carboxyphenylpropionamide {2 g., $[\alpha]_{5893}$ − 51·3° in ethyl alcohol, prepared from *l*-(−)α-*p*-toluenesulphonoxypropionic acid with $[\alpha]_{5780}$ − 29·9° in methyl alcohol}, aniline (1·7 g.), absolute alcohol (20 c.c.), and lithium chloride (1 g.) were heated under reflux for 3 hours. The resulting *d*-(+)α-chloro-*N*-*p*-carboxyphenylpropionamide, crystallised from alcohol, had m. p. 230—233°, $[\alpha]_{5893}$ + 18·0° (*l*, 2; *c*, 4·1640) in ethyl alcohol.

d-(+)*α-Chloro*-N-p-*carboxyphenylpropionamide from* d-(+)*α-Chloropropionyl Chloride*.—*d*-α-Chloropropionyl chloride (2·5 g.; preparation, see p. 308), dissolved in dry ether, was triturated with *p*-aminobenzoic acid (7 g.). The resulting *d*-(+)α-chloro-*N*-*p*-carboxyphenylpropionamide after crystallisation from alcohol had $[\alpha]_{5893}$ + 19·7° (*l*, 2; *c*, 4·424) in ethyl alcohol and m. p. 232°, either alone or when mixed with the α-chloro-amide prepared by the interaction of lithium chloride with either *l*-(−)α-*p*-toluenesulphonoxy-*N*-*p*-carboxyphenylpropionamide or its aniline salt.

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67. *Nitro- and Amino-3-arylphthalaz-4-ones, and Corresponding 1-Methyl Compounds.*

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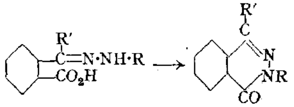
As a preliminary to other projected work, it was necessary to prepare and characterise as reference compounds the series of nitro- and amino-3-arylphthalaz-4-ones, and the corresponding 1-methyl compounds, now described. The opportunity was taken to study also the stabilities of the intermediate hydrazones (I, or its lactone form) and their relative ease of conversion into the nitro-3-arylphthalaz-4-ones (II) under standard conditions.

(I.)  (II.)

(R = nitroaryl; R′ = H or Me)

o-Phthalaldehydic acid was condensed with nitroarylhydrazines, and ring closure of the resulting *o*-carboxybenzaldehydenitroarylhydrazones (I; R′ = H) to the nitro-3-arylphthalaz-4-ones (II; R′ = H) effected in various ways (cf. Racine, *Annalen*, 1887, **239**, 86; Rowe and co-workers, J., 1928, 2551, 2557; 1932, 475). Similarly, acetophenone-*o*-carboxylic acid gave nitro-3-aryl-1-methylphthalaz-4-ones (II; R′ = Me) *via* the *o*-carboxyacetophenonenitroarylhydrazones (I; R′ = Me) (cf. Rowe and co-workers, J., 1931, 1920; 1935, 1135).

The stabilities of the intermediate hydrazones (I; R′ = H or Me) vary considerably with the position of substituents in the 3-phenyl nucleus. Thus, the comparative stabilities are in the order R = 2′-nitrophenyl > 2′-halogeno- and 2′ : 6′-dihalogeno-4′-nitrophenyl > 4′-nitro-2′-methylphenyl > 4′-nitrophenyl > 3′-nitrophenyl. Similar retarding effects of *o*-substituents in a phenyl side-chain on formation of six-membered rings were observed with phthalylnitroarylhydrazides (J., 1935, 1810) and with sodium benzaldehydenitroaryl-

hydrazone-ω-sulphonate-2-β-acrylic acids (*J.*, 1935, 1796). *In general, the hydrazones (I; R′ = H) are more stable than the corresponding hydrazones (I; R′ = Me), e.g., some conditions which converted the latter into the nitro-3-aryl-1-methylphthalaz-4-ones in excellent yields caused no, or only partial, ring closure with most of the former examined. A simple method of preparing large quantities of (II; R′ = H or Me), applicable in most cases with good results, is to dissolve (I; R′ = H or Me) in cold concentrated sulphuric* acid and leave the solution over-night, but the behaviour of (I; R′ = H, R = 2′:6′-*dibromo-4′-nitrophenyl) was exceptional, as it was unaltered by this treatment.*

The nitro-compounds (II; R′ = H or Me) are more stable than the corresponding 1-ones and, unlike the latter, neither form salts with mineral acids nor dissolve in aqueous alkalis, although they dissolve slowly on boiling with aqueous-alcoholic sodium hydroxide and then give a highly coloured layer on addition of acetone.

Amino-3-aryl-1-methylphthalaz-4-ones are obtained by reducing (II; R′ = Me) with aqueous-alcoholic sodium sulphide, but amino-3-arylphthalaz-4-ones in most cases are best prepared from (I; R′ = H) with aqueous sodium sulphide, which effects both ring closure and reduction.

Experimental.

o-*Carboxybenzaldehydenitroarylhydrazones* (I; R′ = H).—These compounds (or their lactone forms) were readily prepared by refluxing a mixture of alcoholic solutions of equimolecular proportions of *o*-phthalaldehydic acid and the appropriate nitroarylhydrazine (cf. J., 1928, 2555).

Methods of converting (I) *into Nitro-3-arylphthalaz-4-ones* (II; R′ = H).—In all cases 1 g. of (I) was used. (i) Heating at 20° below the m. p. of the corresponding compound (II) for 5 minutes; refluxing with (ii) alcohol (20 c.c.) for 1 hour, or (iii) glacial acetic acid (10 c.c.) for ½ hour, or (iv) nitrobenzene (10 c.c.) for ½ hour, or (v) amyl alcohol (10 c.c.), saturated with dry hydrogen chloride, for 1 hour, or (vi) acetic anhydride (5 c.c.) for 10 minutes, or (vii) acetic anhydride (10 c.c.) and pyridine (1 c.c.) for 3 hours; (viii) dissolution in cold concentrated sulphuric acid (10 c.c.), the solution being left over-night. Any unchanged (I) was extracted with cold aqueous sodium carbonate solution, or with cold sodium hydroxide solution when (I) was not very soluble in the former.

Amino-3-arylphthalaz-4-ones (II; R′ = H, R = aminoaryl).—Except where R = 3′-aminophenyl (see below), these compounds were best made from (I), rather than from (II; R = nitroaryl). A suspension of (I) (10 g.) in water (250 c.c.) was heated with sodium sulphide crystals (80 g.) in water (100 c.c.) at 50—60° until the bluish-red colour of the solution changed to orange-yellow or yellow and almost colourless crystals had separated.

o-*Carboxybenzaldehyde-2′-nitrophenylhydrazone* (I; or its lactone form) crystallised from alcohol in bright orange needles, m. p. 229° (refluxed for ½ hour; yield, 85%) (Found: N, 14·8. $C_{14}H_{11}O_4N_3$ requires N, 14·7%), soluble in cold sodium carbonate or hydroxide solution with a violet colour. Conversion into (II; R = 2′-nitrophenyl): Methods (i) to (v) nil; (vi) 90%; (vii) and (viii) 95%.

2′-*Nitro-3-phenylphthalaz-4-one* (II) crystallised from benzene or glacial acetic acid in colourless prisms, m. p. 201° (Found: C, 63·25; H, 3·7; N, 16·0. $C_{14}H_9O_3N_3$ requires C, 62·9; H, 3·4; N, 15·7%), insoluble in aqueous alkalis and hydrochloric acid. This compound and its analogues described subsequently were best prepared by method (viii), unless otherwise stated.

2′-*Amino-3-phenylphthalaz-4-one* crystallised from aqueous alcohol in colourless needles, m.p. 184° (yield, 4 g.; 48·1%) (Found: C, 70·8; H, 4·4; N, 17·8. $C_{14}H_{11}ON_3$ requires C, 70·9; H, 4·6; N, 17·7%); the *acetyl* derivative crystallised from aqueous alcohol in colourless needles, m. p. 237° (Found: N, 15·3. $C_{16}H_{13}O_2N_3$ requires N, 15·05%).

I; R = 3′-*Nitrophenyl* (cf. J., 1928, 2563) (refluxed for 5 minutes; yield, 71%). Conversion into (II; R = 3′-nitrophenyl): Method (i) complete; (ii) 16%; (iii) to (viii) complete.

II; R = 3′-*Aminophenyl*.—In this case, treatment of (I) with aqueous sodium sulphide merely gave (II; R = 3′-nitrophenyl) in a form which was not reduced by prolonged boiling. Reduction was best effected by refluxing a fine suspension of (II; R = 3′-nitrophenyl) (4 g.) in water (100 c.c.) and alcohol (100 c.c.) with sodium sulphide crystals (30 g.) for 20 minutes (yield, 2·3 g.; 64·8%). The *acetyl* derivative of 3′-amino-3-phenylphthalaz-4-one (*loc. cit.*) crystallised from aqueous alcohol in colourless plates, m. p. 225° (Found: N, 15·2%).

I; R = 4′-*Nitrophenyl* (cf. J., 1928, 2555) (refluxed for 5 minutes; yield, 92%). Conversion into (II; R = 4′-nitrophenyl): Method (i) complete, (ii) 5%; (iii) to (viii) complete.

II; R = *4′-Aminophenyl* (*loc. cit.*) (yield, 4·1 g.; 49·3%).

I; R = *4′-Nitro-2′-methylphenyl* (cf. J., 1932, 482) (refluxed for ½ hour; yield, 87%). Conversion into (II; R = 4′-nitro-2′-methylphenyl): Methods (i) and (ii) nil; (iii) 57%; (iv) 31%; (v) 85%; (vi) 71%; (vii) 95%; (viii) 83%.

II; R = *4′-Amino-2′-methylphenyl* crystallised from aqueous alcohol in colourless needles, m. p. 187—188° (yield, 7·5 g.; 89·3%) (Found: N, 16·8. $C_{15}H_{13}ON_3$ requires N, 16·7%); the *acetyl* derivative crystallised from aqueous alcohol in colourless needles, m. p. 214° (Found: N, 14·5. $C_{17}H_{15}O_2N_3$ requires N, 14·3%).

I; R = *2′-Chloro-4′-nitrophenyl* crystallised from alcohol in small yellow needles, m. p. 229° (refluxed for 10 minutes; yield, 75%) (Found: N, 13·3. $C_{14}H_{10}O_4N_3Cl$ requires N, 13·1%), soluble in sodium carbonate and hydroxide solutions with orange-red and deep bluish-red colours, respectively. Conversion into (II; R = 2′-chloro-4′-nitrophenyl): Methods (i) to (v) nil; (vi) 32%; (vii) 99%; (viii) 70%.

II; R = *2′-Chloro-4′-nitrophenyl*, best prepared by method (vi) but refluxing for 3 hours, crystallised from glacial acetic acid or alcohol in colourless prisms, m. p. 171° (Found: N, 13·9. $C_{14}H_8O_3N_3Cl$ requires N, 13·9%), insoluble in cold aqueous alkalis, but soluble in hot aqueous-alcoholic sodium hydroxide with a bluish-red colour.

II; R = *2′-Chloro-4′-aminophenyl* crystallised from aqueous alcohol in colourless needles, m. p. 186° (yield, 6·1 g.; 71·8%) (Found: N, 15·6. $C_{14}H_{10}ON_3Cl$ requires N, 15·45%); the *acetyl* derivative crystallised from aqueous alcohol in colourless needles, m. p. 247° (Found: N, 13·6. $C_{16}H_{12}O_2N_3Cl$ requires N, 13·4%).

I; R = *2′ : 6′-Dichloro-4′-nitrophenyl* crystallised from alcohol in orange-yellow needles, m. p. 225—226° (refluxed for 10 minutes; yield, 85%) (Found: N, 11·7. $C_{14}H_9O_4N_3Cl_2$ requires N, 11·85%), soluble in sodium carbonate and hydroxide solutions with orange-red and intense reddish-violet colours, respectively. Conversion into (II; R = 2′: 6′-dichloro-4′-nitrophenyl): Methods (i) to (v) nil; (vi) 70%; (vii) 93%; (viii) 82%.

II; R = *2′ : 6′-Dichloro-4′-nitrophenyl*, prepared in the same way as the 2′-chloro-analogue, crystallised from glacial acetic acid in small colourless prisms, m. p. 179° (Found: Cl, 21·1. $C_{14}H_7O_3N_3Cl_2$ requires Cl, 21·1%), soluble in boiling aqueous-alcoholic sodium hydroxide with a deep red colour.

II; R = *2′ : 6′-Dichloro-4′-aminophenyl* crystallised from aqueous alcohol in colourless prisms, m. p. 226° (yield, 3·8 g.; 44%) (Found: N, 13·8; Cl, 23·2. $C_{14}H_9ON_3Cl_2$ requires N, 13·7; Cl, 23·2%); the *acetyl* derivative crystallised from aqueous alcohol in colourless needles, m. p. 281° (Found: N, 12·1. $C_{16}H_{11}O_2N_3Cl_2$ requires N, 12·05%).

I; R = *2′-Bromo-4′-nitrophenyl* crystallised from alcohol in yellow needles, m. p. 204° (refluxed for ½ hour; yield, 86%) (Found: N, 11·7. $C_{14}H_{10}O_4N_3Br$ requires N, 11·5%), soluble in sodium carbonate and hydroxide solutions with orange-red and reddish-violet colours, respectively. Conversion into (II; R = 2′-bromo-4′-nitrophenyl): Methods (i) to (iii) nil; (iv) 31%; (v) 23%; (vi) 94%; (vii) and (viii) 96%.

II; R = *2′-Bromo-4′-nitrophenyl* crystallised from glacial acetic acid in colourless prisms, m. p. 154° (Found: C, 48·3; H, 2·5; Br, 23·4. $C_{14}H_8O_3N_3Br$ requires C, 48·55; H, 2·3; Br, 23·1%), soluble in boiling aqueous-alcoholic sodium hydroxide with a bluish-red colour.

II; R = *2′-Bromo-4′-aminophenyl* crystallised from aqueous alcohol in colourless prisms, m. p. 203° (yield, 5·3 g.; 61·1%) (Found: C, 53·4; H, 3·4. $C_{14}H_{10}ON_3Br$ requires C, 53·2; H, 3·2%); the *acetyl* derivative crystallised from aqueous alcohol in small colourless prisms, m. p. 251° (Found: N, 12·0. $C_{16}H_{12}O_2N_3Br$ requires N, 11·7%).

I; R = *2′ : 6′-Dibromo-4′-nitrophenyl* crystallised from alcohol in brownish-yellow needles, m. p. 220° (refluxed for 10 minutes; yield, 86%) (Found: Br, 36·0. $C_{14}H_9O_4N_3Br_2$ requires Br, 36·1%), soluble in sodium carbonate and hydroxide solutions with yellow and deep bluish-violet colours, respectively. Conversion into (II; R = 2′ : 6′-dibromo-4′-nitrophenyl): Methods (i) and (ii) nil; (iii) 36%; (iv) 40%; (v) 92%; (vi) 81%; (vii) 96%; (viii) nil.

II; R = *2′ : 6′-Dibromo-4′-nitrophenyl*, best prepared by method (vi) but refluxing for 2 hours, crystallised from alcohol in colourless prisms, m. p. 190° (Found: N, 9·8; Br, 37·9. $C_{14}H_7O_3N_3Br_2$ requires N, 9·9; Br, 37·65%).

II; R = *2′ : 6′-Dibromo-4′-aminophenyl* crystallised from aqueous alcohol in colourless prisms, m. p. 255° (yield, 5 g.; 56·1%) (Found: N, 10·8; Br, 40·5. $C_{14}H_9ON_3Br_2$ requires N, 10·6; Br, 40·5%); the *acetyl* derivative crystallised from aqueous alcohol in small colourless prisms, m. p. 257° (Found: N, 9·6. $C_{16}H_{11}O_2N_3Br_2$ requires N, 9·6%).

o-Carboxyacetophenonenitroarylhydrazones (I; R′ = Me).—These compounds (or their lactone forms) were prepared by adding a solution of the appropriate nitroarylhydrazine in alcohol

(sufficient to prevent precipitation of the unaltered hydrazine) to an aqueous solution of a equimolecular proportion of acetophenone-o-carboxylic acid at about 70°, unless otherwise stated (cf. J., 1931, 1923).

Conversion of (I) into Nitro-3-aryl-1-methylphthalaz-4-ones (II; R′ = Me).—Methods (i) to (viii) as described for the unmethylated compounds (p. 312) were used.

Amino-3-aryl-1-methylphthalaz-4-ones (II; R′ = Me, R = aminoaryl).—These were prepared satisfactorily in all cases from finely divided (II; R = nitroaryl).

o-*Carboxyacetophenone*-o-*nitrophenylhydrazone* (I; or its lactone form) (*loc. cit.*). Conversion into (II; R = 2′-nitrophenyl): Method (i) nil; (ii) 6%; (iii) 60%; (iv) to (viii) almost complete.

II; R = 2′-*Aminophenyl*.—(II; R = 2′-nitrophenyl) (5 g.), sodium sulphide crystals (50 g.), water (125 c.c.), and alcohol (125 c.c.) were refluxed for 1 hour. *2′-Amino-3-phenyl-1-methylphthalaz-4-one* crystallised from alcohol in pale yellow needles, m. p. 239° (yield, 3·2 g.; 71·6%) (Found: N, 16·4. $C_{15}H_{13}ON_3$ requires N, 16·7%); the *acetyl* derivative crystallised from alcohol in colourless needles, m. p. 241° (Found: N, 13·95. $C_{17}H_{15}O_2N_3$ requires N, 14·3%).

I; R = 3′-*Nitrophenyl*, when the condensation was carried out at 15—20°, separated as a bright orange, amorphous powder, which was very unstable and did not melt, but became colourless at 115°, owing to formation of (II; R = 3′-nitrophenyl) (*loc. cit.*), and then melted at 167° (yield, 82%) (Found: N, 14·0. $C_{15}H_{13}O_4N_3$ requires N, 14·05%); it was soluble in cold sodium carbonate and hydroxide solutions with orange colours. Conversion into (II; R = 3′-nitrophenyl): Method (i) complete; (ii) 78%; (iii) to (viii) complete.

II; R = 3′-*Aminophenyl*, prepared in the same way as the 2′-isomeride, but with sodium sulphide crystals (25 g.) and refluxing for 3 hours, crystallised from alcohol in almost colourless prisms, m. p. 173° (yield, 2·5 g.; 56%) (Found: N, 16·9%); the *acetyl* derivative crystallised from alcohol in colourless prisms, m. p. 220° (Found: N, 14·5%).

I; R = 4′-*Nitrophenyl* (*loc. cit.*). Conversion into (II; R = 4′-nitrophenyl): Method (i) complete; (ii) 71%; (iii) 85%; (iv) to (viii) complete.

II; R = 4′-*Aminophenyl*, best prepared from (I; R = 4′-nitrophenyl) (5 g.), sodium sulphide crystals (40 g.), and water (40 c.c.), heated at 50° for 3 hours, crystallised from alcohol in almost colourless, stout prisms, m. p. 206—207° (yield, 2·8 g.; 66·7%) (Found: C, 71·3; H, 5·4; N, 16·9. $C_{15}H_{13}ON_3$ requires C, 71·7; H, 5·2; N, 16·7%); the *acetyl* derivative crystallised from alcohol in colourless needles, m. p. 252° (Found: N, 14·0%).

I; R = 4′-*Nitro-2′-methylphenyl*, when the condensation was carried out at 5—10°, separated as a bright yellow powder, m. p. 145° (Found: N, 13·3. $C_{16}H_{15}O_4N_3$ requires N, 13·4%), soluble in cold sodium carbonate and hydroxide solutions with orange and deep red colours, respectively. Conversion into (II; R = 4′-nitro-2′-methylphenyl): Method (i) nil; (ii) 29%; (iii) 72%; (iv) to (viii) complete.

II; R = 4′-*Nitro-2′-methylphenyl* crystallised from glacial acetic acid in colourless prisms, m. p. 178° (Found: C, 65·4; H, 4·5; N, 14·2. $C_{16}H_{13}O_3N_3$ requires C, 65·1; H, 4·4; N, 14·2%), sparingly soluble in boiling aqueous-alcoholic sodium hydroxide with a red colour, converted into bluish-red on addition of acetone.

II; R = 4′-*Amino-2′-methylphenyl*, prepared in the same way as the 2′-amino-analogue, but with sodium sulphide crystals (25 g.), water (140 c.c.), and alcohol (140 c.c.), and refluxing for 2 hours, crystallised from alcohol in very pale yellow prisms, m. p. 191° (yield, 2·6 g.; 57·9%) (Found: N, 15·95. $C_{16}H_{15}ON_3$ requires N, 15·85%); the *acetyl* derivative crystallised from alcohol in small colourless prisms, m. p. 235° (Found: N, 14·0. $C_{18}H_{17}O_2N_3$ requires N, 13·7%).

I; R = 2′-*Chloro-4′-nitrophenyl* crystallised from alcohol in orange-yellow needles, m. p. 160° (Found: N, 12·9. $C_{15}H_{12}O_4N_3Cl$ requires N, 12·6%), soluble in sodium carbonate and hydroxide solutions with a red colour. Conversion into (II; R = 2′-chloro-4′-nitrophenyl): Method (i) nil; (ii) 4%; (iii) to (viii) complete.

II; R = 2′-*Chloro-4′-nitrophenyl* crystallised from alcohol in small colourless prisms, m. p. 206° (Found: C, 57·0; H, 3·3; N, 13·1. $C_{15}H_{10}O_3N_3Cl$ requires C, 57·05; H, 3·2; N, 13·3%), sparingly soluble in aqueous-alcoholic sodium hydroxide with a cherry-red colour.

II; R = 2′-*Chloro-4′-aminophenyl*, prepared in the same way as the 2′-amino-analogue, but refluxing for 10 minutes, crystallised from alcohol in colourless prisms, m. p. 197° (yield, 2·3 g.; 50·8%) (Found: N, 14·7. $C_{15}H_{12}ON_3Cl$ requires N, 14·7%); the *acetyl* derivative crystallised from alcohol in small colourless prisms, m. p. 247° (Found: N, 12·6. $C_{17}H_{14}O_2N_3Cl$ requires N, 12·8%).

I; R = 2′ : 6′-*Dichloro-4′-nitrophenyl* crystallised from alcohol in small yellow needles, m. p. 135° (yield, 84%) (Found: N, 11·3. $C_{15}H_{11}O_4N_3Cl_2$ requires N, 11·4%). Conversion into (II: R = 2′ : 6′-dichloro-4′-nitrophenyl): Method (i) nil; (ii) 13%; (iii) to (viii) complete.

II; R = 2' : 6'-*Dichloro-4'-nitrophenyl* crystallised from alcohol in small colourless needles or prisms, m. p. 235° (Found: C, 51·0; H, 2·6; Cl, 20·6. $C_{15}H_9O_3N_3Cl_2$ requires C, 51·4; H, 2·55; Cl, 20·3%).

II; R = 2' : 6'-*Dichloro-4'-aminophenyl*, prepared in the same way as the 2'-amino-analogue, but with alcohol (250 c.c.), crystallised from alcohol in small colourless prisms, m. p. 279° (yield, 2·4 g.; 52·5%) (Found: Cl, 22·3. $C_{15}H_{11}ON_3Cl_2$ requires Cl, 22·2%); the *acetyl* derivative crystallised from glacial acetic acid in small colourless needles, m. p. 320° (Found: N, 11·4. $C_{17}H_{13}O_2N_3Cl_2$ requires N, 11·6%).

I; R = 2'-*Bromo-4'-nitrophenyl* (cf. J., 1935, 1137). Conversion into (II; R = 2'-bromo-4'-nitrophenyl): Method (i) nil; (ii) 2%; (iii) to (viii) almost complete.

II; R = 2'-*Bromo-4'-aminophenyl*, prepared in the same way as the 2'-amino-analogue, but with sodium sulphide crystals (25 g.) and refluxing for ½ hour, crystallised from alcohol in almost colourless needles, m. p. 130° (decomp.) after softening at 123° (yield, 2·8 g.; 61·1%) (Found: Br, 23·9. $C_{15}H_{12}ON_3Br$ requires Br, 24·2%); the *acetyl* derivative crystallised from acetic anhydride in small colourless prisms, m. p. 255° (Found: N, 11·3. $C_{17}H_{14}O_2N_3Br$ requires N, 11·3%).

I; R = 2' : 6'-*Dibromo-4'-nitrophenyl* could not be obtained satisfactorily by the use of an aqueous solution of acetophenone-*o*-carboxylic acid. A boiling solution of acetophenone-*o*-carboxylic acid (20 g., colourless needles, m. p. 116°) in alcohol (100 c.c.) was added to a boiling solution of 2 : 6-dibromo-4-nitrophenylhydrazine (28 g.) (J., 1935, 1814) in alcohol (500 c.c.); on cooling, the *hydrazone* crystallised in small, pale yellow needles, m. p. 167° (yield, 35 g.) (Found: N, 9·3. $C_{15}H_{11}O_4N_3Br_2$ requires N, 9·2%). Conversion into (II; R = 2' : 6'-dibromo-4'-nitrophenyl): Method (i) nil; (ii) 18%; (iii) to (viii) almost complete.

II; R = 2' : 6'-*Dibromo-4'-nitrophenyl* crystallised from glacial acetic acid in small colourless prisms, m. p. 237° (Found: C, 41·3; H, 2·3; Br, 36·2. $C_{15}H_9O_3N_3Br_2$ requires C, 41·0; H, 2·05; Br, 36·4%).

II; R = 2' : 6'-*Dibromo-4'-aminophenyl*, prepared in the same way as the 2'-bromo-analogue, but with sodium sulphide crystals (40 g.), crystallised from alcohol in colourless needles, m. p. 274° (yield, 3 g.; 64·4%) (Found: C, 44·2; H, 2·9. $C_{15}H_{11}ON_3Br_2$ requires C, 44·0; H, 2·7%); the *acetyl* derivative crystallised from alcohol in small colourless needles, m. p. 315° (Found: N, 9·4. $C_{17}H_{13}O_2N_3Br_2$ requires N, 9·3%).

The authors are indebted to Dr. A. T. Peters for assistance in the preparation of some of the compounds described.

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68. *Derivatives of 4 : 4'-Diaminodiphenylmethane.*

By G. D. Parkes and R. H. H. Morley.

The action of two molecular proportions of bromine upon 4 : 4'-diacetamidodiphenylmethane yields 3 : 3'-*dibromo-4 : 4'-diacetamidodiphenylmethane*, from which the free base can be obtained on hydrolysis. This base and 4 : 4'-diaminodiphenylmethane can be diazotised and the bisdiazonium salts yield dihydrazines on reduction. These substances show the normal behaviour of arylhydrazines and from them a series of dihydrazones has been prepared, and their properties recorded for reference.

4 : 4'-Diaminodiphenylmethane was prepared (1) by nitration of diphenylmethane and reduction of the 4 : 4'-dinitrodiphenylmethane formed by tin and hydrochloric acid, (2) by the condensation of formaldehyde with aniline in presence of caustic alkali, followed by transformation of the resulting methylenediphenyldi-imide by heating with aniline hydrochloride. The latter is the more convenient and less wasteful process, 186 g. of aniline yielding 150 g. of base as compared with 45 g. of product from 100 g. of diphenylmethane.

3 : 3'-*Dibromo-4 : 4'-diacetamidodiphenylmethane*.—10 G. of 4 : 4'-diacetamidodiphenylmethane and 8 g. of anhydrous sodium acetate were dissolved in boiling glacial acetic acid, and 12 g. of bromine in 20 c.c. of glacial acetic acid added. Bromination proceeded readily,

and after the slight excess of bromine had been boiled off, the mixture was poured on ice. Th 3 : 3′-dibromo-4 : 4′-diacetamidodiphenylmethane (10 g.) obtained crystallised from alcohol in colourless plates, m. p. 198°, easily soluble in glacial acetic acid and moderately soluble in alcohol (Found : Br, 35·7. $C_{17}H_{16}O_2N_2Br_2$ requires Br, 35·9%).

3 : 3′-Dibromo-4 : 4′-dibenzamidodiphenylmethane (11 g.), obtained similarly from 10 g. of 4 : 4′-dibenzamidodiphenylmethane and 11 g. of bromine, crystallised from glacial acetic acid in white prisms, m. p. 217° (Found : Br, 27·9. $C_{27}H_{20}O_2N_2Br_2$ requires Br, 28·1%).

3 : 3′-Dibromo-4 : 4′-diaminodiphenylmethane (14 g.), m. p. 119° (Found : N, 7·8. $C_{13}H_{12}N_2Br_2$ requires N, 7·9%), was prepared by refluxing 50 g. of 3 : 3′-dibromo-4 : 4′-diacetamidodiphenylmethane with 75 c.c. of concentrated hydrochloric acid and 350 c.c. of alcohol for 5 hours; its *dihydrochloride* (35 g.), which separated on cooling, crystallised from hot water in white rhombic plates, m. p. 285° (decomp.) (Found : N, 6·4. $C_{13}H_{12}N_2Br_2$,2HCl requires N, 6·5%).

The position of the bromine atoms in this compound was established by eliminating the amino-groups by the Sandmeyer method or by the action of Fehling's solution on the corresponding dihydrazine, and oxidation of the resulting dibromodiphenylmethane to dibromobenzophenone, which was identical with authentic 3 : 3′-dibromobenzophenone (Dittrich, *Ber.*, 1890, **23**, 3614).

4 : 4′-Dihydrazinodiphenylmethane.—100 G. of 4 : 4′-diaminodiphenylmethane, dissolved in 300 c.c. of concentrated hydrochloric acid and 500 c.c. of water, were diazotised at 0° with 70 g. of sodium nitrite; on addition to a cold saturated aqueous solution of 400 g. of sodium sulphite, the diazosulphonate separated in yellow needles. 100 C.c. of concentrated hydrochloric acid were added and the whole was warmed slowly to 70° while sulphur dioxide was passed in. Another 400 c.c. of concentrated hydrochloric acid were then added; on cooling, 4 : 4′-dihydrazinodiphenylmethane dihydrochloride separated. A solution of this in boiling water was filtered and, after addition of concentrated hydrochloric acid, allowed to cool, the salt separating in colourless plates, very sparingly soluble in hot water. 4 : 4′-Dihydrazinodiphenylmethane (35 g.), obtained from the dihydrochloride in the usual way, crystallised from alcohol in very pale yellow needles, m. p. 141°.

3 : 3′-Dibromo-4 : 4′-dihydrazinodiphenylmethane was prepared similarly, 45 g. of 3 : 3′-dibromo-4 : 4′-diaminodiphenylmethane and 400 g. of sodium sulphite being used; it crystallised from alcohol in almost colourless prisms, m. p. 161° (Found : N, 14·5. $C_{13}H_{14}N_4Br_2$ requires N, 14·5%). The *dihydrochloride* (yield, 10—15 g.) separated from hot dilute hydrochloric acid in colourless plates, m. p. 279° (decomp.) (Found : N, 12·1. $C_{13}H_{14}N_4Br_2$,2HCl requires N, 12·2%).

The following dihydrazones were prepared by warming 1 g. of the appropriate dihydrazine dihydrochloride with a slight excess of the carbonyl compound in alcohol in presence of excess of anhydrous sodium acetate : *4 : 4′-bis-(o-nitrobenzylidenehydrazino)diphenylmethane* (2·2 g.), deep purple-red plates from acetic acid, m. p. 189° (Found : N, 16·9. $C_{27}H_{22}O_4N_6$ requires N, 17·0%); *4 : 4′-bis-(m-nitrobenzylidenehydrazino)diphenylmethane* (2·0 g.), fine red flattened prisms from acetone, m. p. 192° (Found : N, 16·9%); *4 : 4′-bis-(p-nitrobenzylidenehydrazino)-diphenylmethane* (2·2 g.), red irregular plates from acetic acid, m. p. 218° (Found : N, 16·9%); *4 : 4′-bis-salicylidenehydrazinodiphenylmethane* (2·3 g.), buff-yellow, flattened prisms from dioxan or acetic acid, m. p. 252°; the crystals are phototropic, turning red in sunlight; the colour is lost on heating in a steam-oven (Found : N, 12·6. $C_{27}H_{24}O_2N_4$ requires N, 12·75%); *4 : 4′-bis-(β-phenylethylidenehydrazino)diphenylmethane* (4·2 g.), almost white, lustrous plates from benzene, m. p. 174° (Found : N, 12·5. $C_{29}H_{28}N_4$ requires N, 12·65%); *4 : 4′-bis-γ-(phenyl-α-methylallylidenehydrazino)diphenylmethane* (3·8 g.), pale yellow, lustrous, hexagonal plates from benzene, m. p. 222° (Found : N, 11·3. $C_{33}H_{32}N_4$ requires N, 11·55%). For the following, approx. 0·45 g. of the dihydrazine dihydrochloride were used. *3 : 3′-Dibromo-4 : 4′-bis(benzylidenehydrazino)diphenylmethane* (0·2 g.), buff-yellow plates from glacial acetic acid, m. p. 165° (Found : N, 9·8. $C_{27}H_{22}N_4Br_2$ requires N, 9·9%); *3 : 3′-dibromo-4 : 4′-bis-o-nitrobenzylidenehydrazinodiphenylmethane* (0·3 g.), red microscopic needles from glacial acetic acid, m. p. 234°, very sparingly soluble in acetic acid, ethyl acetate, and acetone, and insoluble in alcohol (Found : Br, 24·3. $C_{27}H_{20}O_4N_6Br_2$ requires Br, 24·5%); *3 : 3′-dibromo-4 : 4′-bis-(m-nitrobenzylidenehydrazino)diphenylmethane* (0·3 g.), orange-red powder from benzene, m. p. 278°, insoluble in ethyl acetate, acetic acid, acetone, and alcohol, very sparingly soluble in benzene (Found : Br, 24·4%); *3 : 3′-dibromo-4 : 4′-bis-(p-nitrobenzylidenehydrazino)diphenylmethane* (0·3 g.), red powder from ethyl acetate, m. p. 255° (decomp.), insoluble in acetic acid, alcohol, and benzene, very sparingly soluble in acetone and ethyl acetate (Found : Br, 24·5%); *3 : 3′-dibromo-4 : 4′-bis-salicylidenehydrazinodiphenylmethane* (0·25 g.), buff-yellow powder from

dioxan–alcohol, m. p. 236° (decomp.), insoluble in alcohol, acetic acid, and benzene (Found: N, 9·3. $C_{27}H_{22}O_2N_4Br_2$ requires N, 9·4%); 3 : 3′-*dibromo*-4 : 4′-*bis*-(p-*hydroxybenzylidene-hydrazino*)*diphenylmethane* (0·25 g.), silvery plates (which soon darkened in air) from alcohol, m. p. 238° (decomp.) (Found: N, 9·5%).

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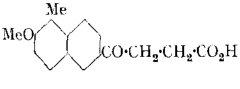
69. *Syntheses in the Phenanthrene Series. Part I. 2-Methoxy-1-methylphenanthrene.*

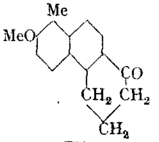
By Peter Hill, W. F. Short, and (in part) Alice Higginbottom.

The object of the present series of investigations was the synthetic preparation of various phenanthrene derivatives related to members of the diterpene group which are under investigation in these laboratories. For the preparation of these compounds, we have extended and adapted the phenanthrene syntheses of (1) Schroeter (*Ber.*, 1929, **62**, 645), the requisite naphthoylpropionic acid being prepared by the modification of Giua's method so successfully exploited by Haworth and his co-workers, and (2) Bogert and Cook, and two new methods for constructing the phenanthrene ring system have been developed.

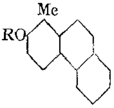
1-Methyl-2-naphthyl methyl ether was obtained by the action of methyl sulphate on the Grignard compound of 1-bromo-2-methoxynaphthalene (Franzen and Stäuble, *J. pr. Chem.*, 1921, **103**, 352), but is more conveniently prepared in quantity from 2 : 2′-dihydroxydi-α-naphthylmethane (Fries and Hübner, *Ber.*, 1906, **39**, 439). This methyl ether and succinic anhydride react in nitrobenzene solution in presence of aluminium chloride to afford β-(2-*methoxy*-1-*methyl*-6-*naphthoyl*)*propionic acid* (I) in 78% yield. The constitution assigned to this acid rests upon the observation that the final product (III; R = H) of the synthesis affords 1-methylphenanthrene when distilled with zinc dust, and the succinic anhydride must therefore have reacted in position 5 or 6. Further, contrary to the statement of Fieser and Peters (*J. Amer. Chem. Soc.*, 1932, **54**, 4351), condensation of β-naphthyl methyl ether with succinic anhydride under similar conditions affords β-(2-methoxy-6-naphthoyl)propionic acid as main product (following paper).



(I.)



(II.)



(III.)

Reduction of the keto-acid by Clemmensen's method furnished γ-(2-*methoxy*-1-*methyl*-6-*naphthyl*)*butyric acid*, from which 1-*keto*-7-*methoxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II) was obtained by the action of stannic chloride. This ketone was reduced by Clemmensen's method, and the product dehydrogenated with selenium to yield 2-*methoxy*-1-*methylphenanthrene* (III; R = Me).

Experimental.

1-*Methyl*-2-*naphthyl Methyl Ether*.—Redistilled methyl sulphate (2 mols.) was added to a Grignard solution prepared from 1-bromo-2-methoxynaphthalene (1 mol.), methyl iodide (1 mol.), magnesium (2 atoms), ether (6 mols.), and an equal volume of dry benzene, and the mixture boiled for 2 hours. Distillation of the product afforded (1) a fraction, b. p. 160—165°/20 mm., m. p. 35—42°, consisting of the required ether and a small quantity of β-naphthyl methyl ether (which may be removed by crystallisation from methyl alcohol), and (2) a small higher-boiling fraction consisting of unchanged 1-bromo-2-methoxynaphthalene.

The preparation and reduction of 2 : 2′-dihydroxydi-α-naphthylmethane were conducted as described by Fries and Hübner (*loc. cit.*), but the tedious separation of the two phenols by means

of boiling water was avoided either by acetylation or by methylation. The mixed acetates, obtained by acetylation with acetic anhydride and sodium hydroxide at 0°, were extracted with boiling light petroleum (b. p. 40—60°), in which only 1-methyl-2-naphthyl acetate (m. p. 65°) dissolved, and the acetate was smoothly hydrolysed by boiling with dilute sodium hydroxide solution. Alternatively, methyl sulphate was rapidly added to a well-stirred solution of the mixed phenols in 15% aqueous potassium hydroxide so that the temperature did not exceed 70°. The portion of the product sparingly soluble in ether consisted of 2 : 2'-dimethoxydi-α-naphthylmethane (m. p. 144°), and distillation of the soluble portion removed the remaining traces of this compound together with some resin and afforded almost pure 1-methyl-2-naphthyl methyl ether (b. p. *ca.* 140°/5 mm.; m. p. 39·5—40·5°).

β-(2-*Methoxy*-1-*methyl*-6-*naphthoyl*)*propionic Acid* (I).—Succinic anhydride (1·2 mols.) and 1-methyl-2-naphthyl methyl ether (1 mol.) were added below 5° to a mechanically stirred solution of aluminium chloride (2 mols.) in nitrobenzene (9 mols.). The mixture was slowly warmed to room temperature with stirring and then kept. The yield of keto-acid after 40 hours was 41%, but could be raised to 63% and 78% by increasing the period of reaction to 3 and 5 days respectively. The solution was decomposed with ice and hydrochloric acid, the nitrobenzene removed in steam and the solid residue washed with water and recrystallised from methyl alcohol. The *acid* (I) was obtained in colourless plates, m. p. 161—162° (Found: C, 70·4; H, 6·0. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

γ-(2-*Methoxy*-1-*methyl*-6-*naphthyl*)*butyric Acid*.—The keto-acid (20 g.) was reduced by gentle boiling for 12 hours with amalgamated zinc (100 g.) and concentrated hydrochloric acid (100 c.c.), and extraction of the acid cake with boiling ligroin furnished the pure *acid*, m. p. 123—123·5°, in 53% yield (Found: C, 74·5; H, 6·9. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%).

1-*Keto*-7-*methoxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II).—The preceding acid (48 g.) was slowly added with mechanical stirring to stannic chloride (96 c.c.) at 40—50°, the temperature being subsequently maintained at 105—110° for 70 minutes. The black product was decomposed with ice and hydrochloric acid and extracted with ether. When the solution was washed with dilute aqueous sodium hydroxide the colour disappeared, and stout yellow prisms of an acid, m. p. 194—195°, were obtained from the alkaline liquor; these were not further investigated. The ethereal solution deposited the ketone on concentration, and a further qnantity was obtained by distilling the mother-liquor under diminished pressure, the fraction, b. p. 210—225°/2 mm., being almost pure. The cyclic *ketone* (II) separated from alcohol in colourless plates, m. p. 107° (Found: C, 80·0; H, 6·75. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). The yield was variable (34—77%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in bright red, stout needles, m. p. 281° (Found: N, 13·2. $C_{22}H_{20}O_5N_4$ requires N, 13·3%).

7-*Methoxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—Reduction of the cyclic ketone with sodium and absolute alcohol yielded an amorphous red substance. The ketone (13·2 g.), amalgamated zinc (67 g.), and concentrated hydrochloric acid (67 c.c.) were boiled for 10 hours, and the product distilled to remove resinous material. The fraction (4·5 g.), b. p. 170—185°/0·2 mm., on recrystallisation from alcohol furnished the pure *tetrahydrophenanthrene*, m. p. 111—112° (Found: C, 85·0; H, 8·15. $C_{16}H_{18}O$ requires C, 85·0; H, 7·95%).

2-*Methoxy*-1-*methylphenanthrene*, obtained by dehydrogenation with selenium, separated from chloroform–light petroleum in small colourless plates, m. p. 161° (Found: C, 86·4; H, 6·2. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). The picrate consisted of orange-red needles, m. p. *ca.* 125—126°, but was too unstable for satisfactory recrystallisation. The methyl ether (1 g.) was smoothly demethylated on boiling (4 hrs.) with hydrobromic acid (45 c.c., *d* 1·5) and acetic acid (45 c.c.); the resulting 2-*hydroxy*-1-*methylphenanthrene* crystallised from methyl alcohol in irregular plates, m. p. 196—197° (Found: C, 86·5; H, 5·8. $C_{15}H_{12}O$ requires C, 86·5; H, 5·7%). Distillation of the phenol (0·4 g.) with a large excess of zinc dust in a combustion tube afforded a semi-solid distillate, which was dissolved in ether, washed with dilute alkali solution, and distilled from sodium under diminished pressure. The distillate melted at 121° after recrystallisation from light petroleum at 0° and did not depress the m. p. of a synthetic specimen of 1-methylphenanthrene (Sherwood and Short, *Rep. Austral. Assoc. Sci.*, 1933, 31, 38). The picrates of the two hydrocarbons also showed no depression in m. p. (137·5°). Small crystals of this picrate are almost pure yellow, but larger crystals have a red tinge.

4-*Methylphenanthrene* (A correction).—Radcliffe, Sherwood, and Short (J., 1931, 2293) published a synthesis of 4-methylphenanthrene and described the hydrocarbon as a solid, m. p. 117°. Soon afterwards, Dr. R. D. Haworth informed us privately that a similar synthesis had yielded 4-methylphenanthrene, m. p. 49—50°. Examination of the original preparations showed that, owing to an unfortunate confusion of specimens, we had ascribed the properties of 1-methyl-

phenanthrene (obtained from podocarpic acid) to 4-methylphenanthrene. The synthetic hydrocarbon melted at 49—50° and Dr. Haworth reported that it did not depress the m. p. of his preparation. He subsequently repeated our synthesis (J., 1932, 1127) and confirmed our description of all the intermediate products.

Our thanks are due to the I. G. Farbenindustrie (Frankfurt) for a gift of 1-methyl-2-naphthol and to the Chemical Society for a research grant.

The College of Technology, Manchester. [*Received, January 7th,* 1936.]

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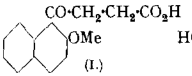
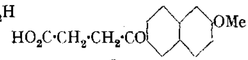
70. *Syntheses in the Phenanthrene Series. Part II. 7-Methoxy-1-methylphenanthrene and a New Route to Phenanthrene.*

By W. F. Short, H. Stromberg, and A. E. Wiles.

Fieser and Peters (*J. Amer. Chem. Soc.*, 1932, **54**, 4351) state that succinic anhydride condenses with β-naphthyl methyl ether in nitrobenzene solution in presence of aluminium chloride to furnish an acid, $C_{15}H_{14}O_4$, m. p. 152°, which was presumed to be β-(2-methoxy-1-naphthoyl)propionic acid (I).



(I.)



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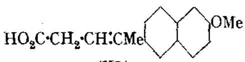
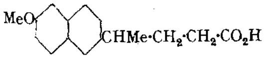
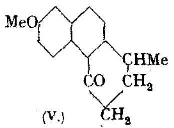


(III.)

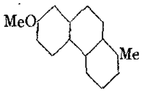
In our hands, these reactants afforded two isomeric ketonic acids, $C_{15}H_{14}O_4$, m. p. 148·5—149° and 136·5—137·5°, produced in the approximate ratio of 9 : 1. Oxidation of these acids with alkaline hypochlorite yielded 2-methoxy-6-naphthoic acid and 2-methoxy-1-naphthoic acid respectively, from which it follows that the acid of higher melting point must be β-(*2-methoxy-6-naphthoyl)propionic acid* (II) and that the acid, m. p. 136·5—137·5°, is β-(*2-methoxy-1-naphthoyl)propionic acid* (I). The acid (I) is the sole product when the reaction is conducted in carbon disulphide solution. Interaction between the ethyl ester of the acid (II) and methylmagnesium iodide in ether–benzene solution afforded γ-(*2-methoxy-6-naphthyl)-Δ^β-pentenoic acid* (III) in 69% yield. On catalytic reduction (platinum oxide and acetic acid at 80°), γ-(*2-methoxy-6-naphthyl)*-n-*valeric acid* (IV) was obtained. The dehydration of (IV) with the formation of 4-keto-7-methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (V) could be effected by means of stannic chloride, but much better yields were obtained by using phosphoric oxide (compare Perkin and Robinson, J., 1907, **91**, 1081). Reduction of the cyclic ketone and dehydrogenation with selenium afforded *7-methoxy-1-methylphenanthrene* (VI).



(IV.)



(V.)

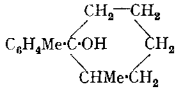


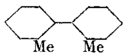
(VI.)

Finally, the demethylation of (VI) by means of hydrobromic–acetic acid yielded *7-hydroxy-1-methylphenanthrene,* which is identical with the phenol obtained by selenium dehydrogenation of the diterpene alcohol, totarol (to be described in a subsequent communication).

The method for the preparation of unsymmetrical derivatives of diphenyl developed by Sherwood, Short, and Stansfield (J., 1932, 1832) may be extended in some cases to the preparation of phenanthrenes and similar condensed ring systems. For instance, 2-methyl*cyclo*hexanone and the Grignard compound prepared from *o*-iodotoluene afford 1-*o*-tolyl-2-methyl*cyclo*hexanol (VII) in 50% yield, and dehydrogenation with sulphur (2 atoms) at 180—250° furnishes 2 : 2′-dimethyldiphenyl (VIII). When the last substance

is heated more strongly with sulphur, phenanthrene is obtained in good yield (compare Berger, *J. pr. Chem.*, 1932, **133**, 338).

(VII.) 

 (VIII.)

This method is suitable for the synthesis of hydrocarbons, but the introduction of a methoxyl group inhibits the final ring closure; *e.g.*, 4-methoxy-2 : 2′-dimethyldiphenyl was easily obtained by the general scheme starting from 2-methyl*cyclo*hexanone and the Grignard compound of 2-bromo-*m*-tolyl methyl ether, but appropriate conditions for conversion into 2-methoxyphenanthrene by dehydrogenation with sulphur or selenium could not be found. For an attempted synthesis of 2-methoxy-1-methylphenanthrene by a similar method, we required 6-bromo-*o*-3-xylenol, and the necessary *o*-3-xylenol was prepared by the following series of reactions: 2-nitro-*m*-tolyl methyl ether (Gibson, J., 1923, **123**, 1273; Haworth and Lapworth, *ibid.*, p. 2993) ⟶ 2-amino-*m*-tolyl methyl ether ⟶ 2-bromo-*m*-tolyl methyl ether ⟶ 3-methoxy-*o*-xylene ⟶ *o*-3-xylenol.

Experimental.

β-(2-*Methoxy*-1-*naphthoyl*)*propionic Acid* (I).—Aluminium chloride (2·2 mols.) was added in small portions with stirring to a solution of β-naphthyl methyl ether (1 mol.) and succinic anhydride (1 mol.) in carbon disulphide, the mixture then being boiled for several hours and worked up in the usual way. The *keto-acid*, recrystallised from benzene–ligroin, had m. p. 136·5—137·5° (Found: C, 69·8; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%). The *ethyl* ester separated from methyl alcohol in colourless plates, m. p. 41—42° (Found: C, 71·0; H, 6·3. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%). The keto-acid (1 g.) and 100 c.c. of alkaline sodium hypochlorite (0·25*M*-NaOCl and 0·5*N*-NaOH) were heated on the water-bath for 20 minutes, then boiled gently for 20 minutes, filtered, and saturated with sulphur dioxide. The precipitated acid, recrystallised from ethyl acetate, melted at 174—175° either alone or after admixture with 2-methoxy-1-naphthoic acid (Fuson, Farlow, and Stehman, *J. Amer. Chem. Soc.*, 1931, **53**, 4101). The methyl esters, prepared by means of diazomethane, melted at 49—49·5° either alone or after admixture. Werner and Seybold (*Ber.*, 1904, **37**, 3661) record m. p. 52°.

β-(2-*Methoxy*-6-*naphthoyl*)*propionic Acid*.—Succinic anhydride (1·1 mols.) and β-naphthyl methyl ether (1 mol.) were added alternately during ½ hour to a mechanically stirred solution of aluminium chloride (2 mols.) in nitrobenzene (8 mols.), cooled in a freezing mixture. The whole was stirred for ½ hour, kept for 100 hours, and then decomposed with ice and hydrochloric acid. Nitrobenzene was removed in steam, and the crude acids isolated with sodium carbonate. The sticky cake was repeatedly extracted with boiling benzene and the extract was recrystallised from methyl alcohol until the m. p. reached *ca.* 135° and then esterified by boiling with 15% alcoholic hydrogen chloride. The crude ester, recrystallised from methyl alcohol, afforded a *solid*, m. p. 107·5—108° (Found: C, 71·3; H, 6·3. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%), and a liquid, which was distilled under diminished pressure. The fraction, b. p. 206—233°/4 mm., was recrystallised from methyl alcohol; it then melted at 41—42° either alone or after admixture with ethyl β-(2-methoxy-1-naphthoyl)propionate (above). The methyl-alcoholic mother-liquors from the recrystallisation of the crude keto-acids were esterified; the fraction, b. p. 206—240°/4 mm., furnished a further quantity of the keto-ester, m. p. 107·5—108°. The *methyl* ester separated from methyl alcohol in plates, m. p. 98° (Found: C, 70·4; H, 6·1. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%). Saponification of these esters afforded β-(2-*methoxy*-6-*naphthoyl*)*propionic acid*, m. p. 148·5—149° after recrystallisation from methyl alcohol (Found: C, 69·9; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%). This is probably the compound assumed by Fieser and Peters (*loc. cit.*), who record m. p. 152°, to be β-(2-methoxy-1-naphthoyl)propionic acid. Oxidation of the acid with alkaline hypochlorite, under the conditions already specified, afforded 2-methoxy-6-naphthoic acid, m. p. 205°, which did not depress the m. p. of an authentic specimen kindly supplied by Dr. R. D. Haworth. A portion of the acid was converted, through the chloride, into 2-methoxy-6-naphthamide, m. p. 213—215° (Fries and Schimmelschmidt, *Ber.*, 1925, **58**, 2835, record m. p. 216°). The total yield of pure ketonic acids was *ca.* 45%.

γ-(2-Methoxy-6-naphthyl)-Δ^β-pentenoic Acid.—Methylmagnesium iodide (from methyl iodide, 8 g.; magnesium, 0·8 g.; and ether, 40 c.c.) was added during 20 minutes with shaking to an ice-cold solution of ethyl β-(2-methoxy-6-naphthoyl)propionate (5 g.) in benzene (210 c.c.) and a little ether. The mixture was boiled under reflux for 1 hour, decomposed with ice and sulphuric acid, and filtered. The grey solid was dissolved in dilute sodium carbonate solution, reprecipitated by acidification, and recrystallised from glacial acetic acid; m. p. 154—157°. A further quantity was obtained from the benzene solution by extraction with dilute sodium carbonate solution, and successive recrystallisation from acetone and ethyl acetate raised the m. p. to 171—171·5° (Found: C, 75·0; H, 6·2. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·25%). The average yield was 69%.

γ-(2-Methoxy-6-naphthyl)-n-valeric Acid.—Hydrogen was passed under slight pressure into a mechanically stirred solution of the unsaturated acid (0·5 g.) in glacial acetic acid (200 c.c.) at 80° in presence of platinum oxide catalyst (0·1 g.). The theoretical quantity of hydrogen was absorbed in 2 hours; the product, isolated in the usual way, crystallised from ligroin in white microscopic needles, m. p. 121·5° (Found: C, 74·1; H, 7·1. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%). The yield was 98%.

4-Keto-7-methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene.—Phosphoric oxide (5 parts) was added in small portions with vigorous shaking to a solution of the saturated acid (1 part) in boiling benzene (15 parts). After boiling for 3 hours, the mixture was decomposed with ice, and the aqueous layer extracted repeatedly with ether. The extract was washed with dilute sodium carbonate solution, which removed a little unchanged acid, and the ketone, isolated by distillation, was obtained in 80% yield as a viscous oil, b. p. 195°/0·8 mm. The 2 : 4-*dinitrophenylhydrazone* separated from toluene–ligroin in red needles, m. p. 241° (decomp.) (Found: C, 62·7; H, 5·2; N, 13·4. $C_{22}H_{20}O_5N_4$ requires C, 62·9; H, 4·8; N, 13·4%).

7-Methoxy-1-methylphenanthrene.—The cyclic ketone was reduced with amalgamated zinc and concentrated hydrochloric acid, and the product dehydrogenated with selenium. The fraction, b. p. 195—200°/0·5 mm., recrystallised from alcohol, formed white plates, m. p. 133·5—134·5° (Found: C, 86·2; H, 6·5. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). The picrate separated from methyl alcohol in red needles, m. p. *ca.* 142°, but was unstable. The methyl ether was smoothly demethylated by boiling hydrobromic–acetic acid; the resulting *7-hydroxy-1-methylphenanthrene* crystallised from benzene in clustered needles, m. p. 190—191° (Found: C, 86·3; H, 5·85. $C_{15}H_{12}O$ requires C, 86·5; H, 5·7%). The *acetate*, m. p. 135·5—136° (Found: C, 81·4; H, 5·6. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%), was oxidised to an orange-yellow *quinone*, m. p. 202—207° (decomp.) (Found: C, 72·7; H, 4·9. $C_{17}H_{12}O_4$ requires C, 72·85; H, 4·3%), which afforded a *quinoxaline*, m. p. 244·5—246·5° (Found: C, 78·65; H, 4·65. $C_{23}H_{16}O_2N_2$ requires C, 78·4; H, 4·5%).

*1-o-Tolyl-2-methyl*cyclo*hexanol.*—*o*-Tolylmagnesium iodide and 2-methyl*cyclo*hexanone reacted under the general conditions specified by Sherwood, Short, and Stansfield (*loc. cit.*) to produce the tertiary *alcohol*, b. p. 153—154°/14 mm., in 50% yield (Found: C, 82·1; H, 9·9. $C_{14}H_{20}O$ requires C, 82·35; H, 9·8%). Dehydrogenation with sulphur (2 atoms) at 180—250° afforded 2 : 2′-dimethyldiphenyl, m. p. 16—17°, which was compared with a specimen produced by Ullmann's method (*Annalen*, 1904, **332**, 38). When 2 : 2′-dimethyldiphenyl (1·4 g.) and sulphur (0·7 g.) were heated in a metal-bath at 270—280°, very little hydrogen sulphide was evolved, but when the temperature was raised so that the mixture distilled, brisk evolution of gas occurred. The distillate solidified immediately and after recrystallisation from alcohol melted at 99° either alone or after admixture with phenanthrene. The picrate, m. p. 145°, caused no depression of the m. p. of phenanthrene picrate. Attempts to convert the carbinol into phenanthrene in one operation by increasing the quantity of sulphur and raising the temperature afforded small yields and the synthesis is most successfully carried out in stages as described above.

6-Bromo-m-tolyl Methyl Ether.—The bromination of *m*-cresol is better effected in acetic acid solution as described by Darzens and Levy (*Compt. rend.*, 1931, **193**, 292) rather than in chloroform (Huston and Hutchinson, *J. Amer. Chem. Soc.*, 1932, **54**, 1504). The yield of pure 6-bromo-*m*-cresol, m. p. 5°, was 55% and 4-bromo-*m*-cresol could not be detected in the product. Methylation with methyl sulphate in 10% sodium hydroxide solution afforded the phenol ether, b. p. 132—135°/25 mm., in satisfactory yield.

*1-(5′-Methoxy-o-tolyl)-2-methyl-Δ^1-*cyclo*hexene.*—The Grignard compound of 6-bromo-*m*-tolyl methyl ether reacted with 2-methyl*cyclo*hexanone (1 mol.) at 0° to afford a mixture from which a fraction, b. p. 154—157°/13 mm., could be isolated by fractionation. Analysis showed that this consisted mainly of the unsaturated *compound*, the carbinol having been dehydrated

during the reaction (Found: C, 81·8; H, 9·1. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·4%. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). The yield was 39%. Dehydrogenation with sulphur at 180—240° afforded 4-methoxy-2 : 2′-dimethyldiphenyl in 52% yield. Demethylation could not be effected with hydrobromic acid, but when the crude methyl ether (3 g.) was boiled for 2 hours with hydriodic acid (4 c.c., *d* 1·7) and acetic acid (6 c.c.), *4-hydroxy-2 : 2′-dimethyldiphenyl*, m. p. 105°, was obtained (Found: C, 84·9; H, 7·25. $C_{14}H_{14}O$ requires C, 84·9; H, 7·1%). The methyl ether, heated with sulphur or selenium under a variety of conditions, was either unchanged or completely destroyed; no 2-methoxyphenanthrene could be detected in the product.

2-Bromo-m-tolyl Methyl Ether.—Sodium hydrosulphite (100 g.) was added during 1½ hours to a boiling mixture of 2-nitro-*m*-tolyl methyl ether (20 g.) (Haworth and Lapworth, *loc. cit.*), alcohol (60 c.c.), and water (100 c.c.). The mixture was then acidified with hydrochloric acid, boiled for 5 minutes, filtered, and made alkaline. Extraction with chloroform furnished 2-amino-*m*-tolyl methyl ether, b. p. 123—130°/18 mm., m. p. 30°, in 67% yield (Gibson, *loc. cit.*, records m. p. 31°). The amine (13·7 g.), dissolved in sulphuric acid (100 c.c.) and water (140 c.c.), was diazotised at 0°, and the solution added to cuprous bromide solution [from copper sulphate 6 g., potassium bromide 6 g., copper powder 3 g., hydrobromic acid (*d* 1·5) 39 c.c., and water 3 c.c.] at 60°. 2-Bromo-*m*-tolyl methyl ether, obtained in 44% yield, was purified by distillation (b. p. 124°/18 mm.), m. p. 38° (Hodgson and Beard, J., 1925, **127**, 498, record m. p. 35·5—36·5°). A small quantity of 2-hydroxy-*m*-tolyl methyl ether, m. p. 41—42° (Majima and Okazaki, *Ber.*, 1916, **49**, 1482), was isolated as by-product.

o-3-Xylenol.—Methyl sulphate (54·5 g.) and ether (150 c.c.) were added during an hour to a Grignard solution prepared from 2-bromo-*m*-tolyl methyl ether (87 g.), magnesium (10·5 g.), and ether (285 c.c.); the mixture was then boiled for an hour and worked up in the usual way. Fractionation of the product afforded 3-methoxy-*o*-xylene, b. p. 85°/18 mm., which was smoothly demethylated by boiling hydrobromic–acetic acid to *o*-3-xylenol, m. p. 73·5—74·5° after crystallisation from alcohol, which did not depress the m. p. of an authentic specimen obtained from the Gesellschaft für Teerverwertung (Duisberg-Meiderich). Bromination of the phenol, dissolved in 10 parts of acetic acid at 0°, furnished 6-bromo-*o*-3-xylenol in 94% yield. This compound melted at 92° as stated by Lockemann and Kuntzmann (*Angew. Chem.*, 1933, **46**, 297) and methylation in 10% alkali solution afforded the methyl ether, b. p. 139—140°/17 mm.

We are indebted to the Chemical Society for a grant.

THE COLLEGE OF TECHNOLOGY, MANCHESTER. [*Received, January 9th*, 1936.]

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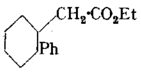
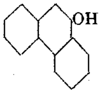
71. *Syntheses in the Phenanthrene Series. Part III. 9-Hydroxyphenanthrene.*

By I. R. SHERWOOD, W. F. SHORT, and J. WOODCOCK.

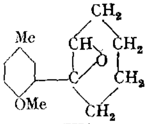
IN this communication we describe a synthesis of 9-hydroxyphenanthrene by an extension of the method employed for the synthesis of members of the diphenyl series (Sherwood, Short, and Stansfield, J., 1932, 1832); we hope to employ it as a model for other syntheses in the phenanthrene group.* 2-Phenyl*cyclo*hexanone (Lévy and Sfiras, *Bull. Soc. chim.*, 1931, **49**, 1834) was condensed with ethyl bromoacetate by the Reformatsky method, and the product dehydrogenated by sulphur to *ethyl diphenylyl-2-acetate* (I). By the action of concentrated sulphuric acid, this ester was converted into 9-hydroxyphenanthrene (II).

(I.) 

 (II.)

* Subsequent to the completion of our experiments, similar phenanthrene and hydrophenanthrene syntheses involving the building of the central nucleus were described by Chatterjee (*J. Indian Chem. Soc.*, 1935, **12**, 591) and Cook, Hewett, and Lawrence (this vol., p. 71).

Similarly, the Grignard compound of 3-bromo-*p*-tolyl methyl ether and *cyclo*hexanone afforded 1-(4'-methoxy-*m*-tolyl)*cyclo*hexanol, which was successively dehydrated to 1-(4'-*methoxy*-m-*tolyl*)-Δ^1-cyclo*hexene* and oxidised to the oxide (III). When the oxide was heated with zinc chloride, isomerisation to 2-(4'-methoxy-*m*-tolyl)*cyclo*hexanone (IV) occurred. The semicarbazone melted at 199—200° and since the isomerisation product did not possess reducing properties the isomeric *cyclo*pentane aldehyde (V) was presumably not formed in this instance.



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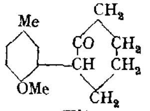

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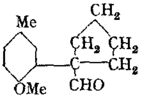

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The ketone (IV) could not be brought into reaction with ethyl bromoacetate and zinc or with ethyl cyanoacetate under any of the standard conditions and alternative methods for introducing the carbon atoms for building up the central nucleus of the phenanthrene ring system are being sought.

Experimental.

*2-Phenyl*cyclo*hexanone*.—1-Phenyl*cyclo*hexanol (Sabatier and Mailhe, *Compt. rend.*, 1904, 138, 1321) was dehydrated to 1-phenyl-Δ^1-*cyclo*hexene, b. p. 136—139°/20 mm., by heating at 150—160° for 1 hour with an equal weight of potassium hydrogen sulphate. The unsaturated hydrocarbon was oxidised to 1-phenyl*cyclo*hexane 1 : 2-oxide, b. p. 120°/10 mm., as described by Nametkin and Iwanov (*Ber.*, 1923, **56**, 1805) and then converted into a mixture of 2-phenyl*cyclo*hexanone, m. p. 62°, and 1-phenyl*cyclo*pentane-1-aldehyde by heating with zinc chloride (Lévy and Sfiras, *loc. cit.*).

Ethyl Diphenylyl-2-acetate.—The Reformatsky reaction between 2-phenyl*cyclo*hexanone (20 g.), ethyl bromoacetate (21·1 g.), and zinc needles (7·5 g.) was carried out in benzene solution (150 c.c.), and the resulting semi-solid mixture of hydroxy and unsaturated esters (12·6 g.), b. p. 155—166°/5 mm., was dehydrogenated by heating at 180—240° for 4 hours with sulphur (2 atoms). Distillation of the product yielded *ethyl diphenylyl-2-acetate* (5·9 g.), b. p. 154—155°/4 mm. (Found : C, 80·1; H, 6·8. $C_{16}H_{16}O_2$ reqnires C, 80·0; H, 6·7%).

9-Hydroxyphenanthrene.—The preceding ester was added gradually with stirring to 85% sulphuric acid, warmed slowly, and heated on the water-bath for 1 hour. The dark solution was cooled, diluted with water, and extracted with ether. The extract was washed with water and dried over magnesium sulphate, the solvent removed, and the residue distilled. The fraction, b. p. 216—225°/5 mm., was converted into the picrate, m. p. 183° after recrystallisation from alcohol (lit., 183°; 185°). Decomposition of the picrate with ammonia afforded 9-hydroxyphenanthrene, m. p. 150—151°, from which the methyl ether, m. p. 97—98°, was prepared. Oxidation of the methyl ether with chromic anhydride in acetic acid solution yielded phenanthraquinone, m. p. 203—204°, identified by conversion into the quinoxaline, m. p. and mixed m. p. 218—219°.

1-(4'-*Methoxy*-m-*tolyl*)-Δ^1-cyclo*hexene*.—Dropwise addition of bromine (1 mol.) to a solution of *p*-tolyl methyl ether (1 mol.) in glacial acetic acid (8 mols.) in presence of iron powder (½ g.), with stirring and cooling in water, afforded 3-bromo-*p*-tolyl methyl ether, b. p. 124—125°/20 mm., in 60% yield. The yield of 1-(4'-methoxy-*m*-tolyl)*cyclo*hexanol, m. p. 77°, obtained by the reaction between the Grignard compound of this ether and *cyclo*hexanone (Sherwood, Short, and Stansfield, *loc. cit.*) was raised to 45% when the experiment was performed on a larger scale. Dehydration of the carbinol (54 g.) with potassium hydrogen sulphate at 150—160° (1 hour) or by boiling for 1 hour with 130 g. of 100% formic acid gave an 80% yield of 1-(4'-*methoxy*-m-*tolyl*)-Δ^1-cyclo*hexene*, b. p. 163°/20 mm. (Found : C, 83·1; H, 9·0. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). Saturation of a cold acetic acid solution of the unsaturated compound with dry hydrogen bromide produced a white unstable solid which fumed in air. After cautious recrystallisation from acetic acid this melted at 58—60° (decomp.) (Found, by titration with alcoholic potash : Br, 26·2. $C_{14}H_{19}OBr$ requires Br, 28·3%).

2-(4'-*Methoxy*-m-*tolyl*)cyclo*hexanone*.—Oxidation of the unsaturated compound with

perbenzoic acid in chloroform solution was complete in 24 hours at 0°. The chloroform solution was repeatedly washed with aqueous sodium carbonate and water, dried over magnesium sulphate, and distilled. The main fraction boiled at 170—200°/26 mm., but there was always a small fraction, b. p. 200—220°/26 mm., containing benzoic acid. The crude oxide was heated to 180° with a fragment of zinc chloride, and the temperature allowed to fall to 150° during 1 hour. Distillation afforded a fraction, b. p. 160—170°/10 mm., which gave a *semicarbazone*, m. p. 199—200° after recrystallisation from methyl alcohol (Found: N, 15·3. $C_{15}H_{11}O_2N_3$ requires N, 15·85%).

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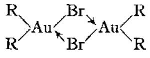
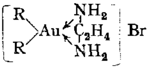
The College of Technology, Manchester. [*Received, January 9th,* 1936.]

72. *The Organic Compounds of Gold. Part VI. Heterocyclic Compounds.*

By Abraham Burawoy and Charles S. Gibson.

The early work on the action of magnesium on αε-dibromopentane in ether (Grignard and Vignon, *Compt. rend.*, 1907, **144**, 358; von Braun and Sobecki, *Ber.*, 1911, **44**, 1918) showed that the resulting solution contained, besides dimagnesium pentamethylene dibromide, magnesium compounds of decamethylene dibromide and higher homologues of the type $Br{\cdot}[CH_2]_{5x}{\cdot}Br$. In spite of the complexity of such a product, von Braun and Sobecki were able to prepare normal products from the interaction of dimagnesium pentamethylene dibromide and certain typical organic compounds. Hilpert and Grüttner (*Ber.*, 1914, **47**, 177, 186) indicated that according as the interaction of magnesium and αε-dibromopentane in ether proceeded rapidly or slowly, the yield of the normal product was 50% or 90%. Heterocyclic compounds of the type $C_5H_{10}{>}XR$, where X = P, Sb, or Bi and R = an alkyl or an aryl group, were prepared by Grüttner and Wiernik (*Ber.*, 1915, **48**, 1473) and, where X = As, by Zappi (*Bull. Soc. chim.*, 1916, **19**, 151) by the action in ethereal solution of the product of the reaction of magnesium and αε-dibromopentane and compounds of the type $RXCl_2$. Under somewhat analogous conditions, using diethyl-lead dichloride and dimethyltin dichloride, Grüttner and Krause (*Ber.*, 1916, **49**, 2666) obtained diethyl*cyclo*pentamethyleneplumbine and Grüttner, Krause, and Wiernik (*Ber.*, **1917**, **50**, 1549) obtained dimethyl- and diethyl-*cyclo*pentamethylenestannines, $C_5H_{10}{>}XR_2$. Bygdèn (*Ber.*, **1915**, **48**, 1236) prepared *cyclo*pentamethylenesilicon dichloride, $C_5H_{10}{>}SiCl_2$, using silicon tetrachloride. All these compounds have definite boiling points and were separated by fractional distillation, and the isolation of derivatives containing ring systems larger than that produced by dimagnesium pentamethylene dibromide either was not attempted or was unsuccessful.

Since organo-gold compounds of type (I) cannot be distilled even under highly reduced

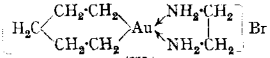
(I.)   (II.)

pressure and are not sufficiently stable, when solid at the ordinary temperature, to allow of prolonged recrystallisation, any organo-gold compounds formed by the mixture produced by the action of magnesium on αε-dibromopentane in ethereal solution have to be isolated in the form of their co-ordination compounds (those with ethylenediamine being the most easily accessible), which, corresponding to compounds of type (I), are of type (II).

In the first experiments (1931—32), carried out by one of the authors (C. S. G.) and Mr. W. M. Colles, the reaction between magnesium and αε-dibromopentane was performed rapidly and this mixture was allowed to react with hydrobromoauric acid in ethereal solution under conditions similar to those obtaining in the earlier investigations (J., 1930, 2531; 1931, 2407). The only organo-gold compound isolated was a colourless crystalline

salt, becoming slightly coloured on exposure to light, and having the molecular formula $C_{12}H_{28}N_2BrAu$. Since Grüttner and collaborators obtained only *cyclo*pentamethylene derivatives, this compound was believed to be a *cyclo*pentamethylene derivative and was described as ethylenediamino*spiro*bis(pentamethylene)gold bromide. The colourless oily product, which cannot be purified, obtained from this by treatment in aqueous solution with hydrobromic acid was described as *spiro*bis(pentamethylene)gold bromide (Gibson, *Nature*, 1933, **131**, 130). The erroneous conclusions as to the constitutions of these two compounds are now corrected in the light of further experimental work.

In the second series of experiments, commenced in 1934, with pyridinotrichlorogold (J., 1931, 2407; 1934, 860) and the mixture obtained by the slow reaction between αε-dibromopentane and magnesium, not only was the salt $C_{12}H_{28}N_2BrAu$ again isolated in the largest amount, but also a colourless salt, $C_7H_{18}N_2BrAu$, was obtained in less quantity. The latter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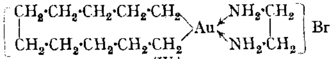
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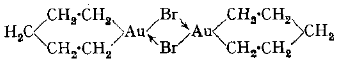
is obviously *ethylenediamino*cyclo*pentamethylenegold bromide* (III) and the compound $C_{12}H_{28}N_2BrAu$ must be *ethylenediamino*cyclo*decamethylenegold bromide* (IV), the composition being analogous to that of the *cyclo*pentamethylene compound. These two organo-gold compounds, like all such compounds containing tervalent gold, obey the rules that the gold atom has an octet of electrons and an effective atomic number of 84.

In addition to these two compounds, analytical evidence was obtained of the existence of gold compounds having a higher carbon content, and therefore presumably containing larger heterocyclic rings, together with a mixture of hydrocarbons, from which *n*-triacontane was isolated.

Apart from the isolation of these two derivatives of heterocyclic gold compounds, this work emphasises the complex nature of the mixture resulting from the interaction of magnesium with αε-dibromopentane in ethereal solution under various conditions.

On acidification with hydrobromic acid of an aqueous solution of ethylenediamino*cyclo*decamethylenegold bromide (IV), a colourless oil separates. This is soluble in ligroin, but the residue remaining after evaporation decomposes too quickly to allow of its identification. When ethylenediamino*cyclo*pentamethylenegold bromide (III) is submitted to the same process, a colourless crystalline product of empirical formula $C_5H_{10}BrAu$ is obtained. This also is unstable and undergoes extensive decomposition in a closed apparatus in three days. The compound is insoluble in water and sparingly soluble in alcohol and *cyclo*hexane. It is readily soluble in chloroform, bromoform, carbon tetrachloride, ether, and benzene, but undergoes rapid decomposition in the solutions. Its molecular weight in bromoform was 434·3 after five minutes (calc. for $C_5H_{10}BrAu$, 347·2), 393 after 10 minutes, and 369 after 15 minutes. In view of the known constitution of dialkylmonobromogold compounds (*J.*, *1930*, 2531) and the above molecular-weight determinations it is reasonable


(V.)

to conclude that the above substance is *bis*(cyclo*pentamethylenemonobromogold*) (V). From this it follows that the compound obtained from (IV) by the action of hydrobromic acid would, if isolated, be bis(*cyclo*decamethylenemonobromogold).

Experimental.

*First Series of Experiments.—Ethylenediamino*cyclo*decamethylenegold bromide* (IV). The filtered ethereal solution obtained by allowing pure αε-dibromopentane (Johnson, J., 1933, 1531) (53 g.; 3 mols.) to react as completely as possible with magnesium (11 g.) in ether (150 c.c.) during 1½ hours—the conditions for the rapid reaction—was added to an ethereal solution (250 c.c.) of hydrobromoauric acid (Gibson and Colles, J., 1931, 2407), prepared from gold tribromide

(33 g.), the reaction conditions described by Gibson and Simonsen (J., 1930, 2531) being maintained. After 3 hours, the mixture was treated and stirred with ice-water (50 c.c.) and then with acetic acid (10 c.c.) and water (40 c.c.). The liquids were filtered rapidly from precipitated gold and the separated ethereal solution was washed rapidly with water until free from water-soluble gold compound and then treated with ethylenediamine until, after thorough mixing, no further colourless precipitate was formed. The mixture was extracted many times with small quantities of water until all the precipitate had dissolved. (The washed ethereal solution contained hydrocarbons, from which *n*-triacontane, m. p. 66°, was isolated.) The combined aqueous solutions after acidification with hydrobromic acid (cloudy precipitate) were rapidly extracted with ether, the ethereal solution again treated with ethylenediamine, and the water-soluble product extracted as before. This procedure is necessary to separate hydrocarbon by-products as completely as possible; the various operations and especially the extractions with ether must be carried out rapidly, otherwise a considerable amount of decomposition of the "parent" gold compound takes place. The aqueous solution was evaporated under reduced pressure at the ordinary temperature, and the almost colourless, crystalline salt (0·08 g.) separated. The combined product from four such experiments was recrystallised three times from warm water (80°), *ethylenediamino*cyclo*decamethylenegold bromide* being obtained in small colourless needles, which darkened a little on standing and decomposed slowly at 150° and rapidly at 180° (Found: C, 30·5, 30·5; H, 6·0, 5·85; N, 5·7, 6·0; Br, 17·7, 17·5; Au, 40·4, 40·1. $C_{12}H_{28}N_2BrAu$ requires C, 30·2; H, 5·9; N, 5·9; Br, 16·7; Au, 41·3%). The compound (IV) is readily soluble in ethyl alcohol and in warm water; it is sparingly soluble in cold water. In spite of its being a salt, it is difficult, especially when only small quantities are available, to eliminate traces of hydrocarbon by-products.

Second Series of Experiments.—The Grignard reagent was prepared by allowing magnesium to react slowly with the corresponding quantity of pure αε-dibromopentane, the ethereal solution being finally gently heated for 7 hours—the conditions of the slow reaction.

To a mechanically stirred suspension of pyridinotrichlorogold (40 g.) in dry pyridine (300 c.c.), a filtered solution prepared as described above from magnesium (10·2 g.), αε-dibromopentane (60 g.; 2½ mols.), and ether (100 c.c.) was added during 15 minutes, the whole being cooled in a freezing mixture. The mixture was stirred during a further 30 minutes and water (100 c.c.) at 0° was then added, followed by ligroin (b. p. 40—60°, 200 c.c.) and by hydrobromic acid (*d* 1·49, 450 c.c.), added at such a rate that the temperature did not rise above 30°. The mixture was stirred during another 30 minutes and then filtered from precipitated gold and unchanged pyridinotrichlorogold. The ligroin solution was separated, the aqueous solution extracted three times with fresh ligroin, and the combined ligroin solutions, after being washed with water, were shaken with ethylenediamine until no further colourless precipitate was produced. The precipitate was collected, washed by decantation with fresh ligroin, and finally separated from a small quantity of ligroin by evaporation at the ordinary temperature.

The product from four such preparations was dissolved in warm 20% aqueous alcohol and, after standing at the ordinary temperature, the solution (A) was decanted from an oily precipitate. This was dissolved in the minimum quantity of alcohol, and the filtered solution evaporated under reduced pressure over sulphuric acid. The residue (2 g.) was dissolved in alcohol and precipitated with ether. The colourless precipitate was recrystallised from warm aqueous alcohol, a mixture of ethylenediamine derivatives of organic gold compounds being obtained [Found: C, 39·9; H, 6·8; Au, 33·2. Calc. for $C_7H_{18}N_2BrAu$ (ethylenediamino*cyclo*pentamethylenegold bromide): C, 20·6; H, 4·4; Au, 48·4%. Calc. for $C_{12}H_{28}N_2BrAu$ (*cyclo*decamethylene compound): C, 30·2; H, 5·9; Au, 41·3%. Calc. for $C_{17}H_{38}N_2BrAu$ (*cyclo*pentadecamethylene compound): C, 37·3; H, 7·0; Au, 36·0%].

On evaporation, under reduced pressure, of filtrate (A) at about 60° and finally to small bulk at the ordinary temperature a crystalline material (10 g.) was obtained, which was recrystallised twice from warm alcohol, giving small colourless plates of pure *ethylenediamino*cyclo*pentamethylenegold bromide* (III), decomp. 150°, soluble in water and sparingly soluble in cold alcohol (Found: C, 21·0; H, 4·4; N, 7·35; Br, 20·1; Au, 48·4. $C_7H_{18}N_2BrAu$ requires C, 20·6; H, 4·4; N, 6·9; Br, 19·6; Au, 48·4%).

By the careful addition of water to the alcoholic filtrates obtained in the purification of compound (III), colourless precipitates were obtained. These were recrystallised several times from aqueous alcohol and finally from warm water (80°), the products being analysed at each stage [Found: (i) C, 32·9; H, 6·3; Au, 38·5; (ii) C, 32·6; H, 6·4; Au, 39·3; (iii) C, 31·6; H, 6·2; Au, 40·1; (iv) C, 31·6; H, 6·1; Au, 39·7; (v) C, 31·3; H, 6·0; Au, 39·8; (vi) C, 30·85; H, 6·1; Au, 40·25%]. They approximate in composition to ethylenediamino*cyclo*decamethyl-

enegold bromide (IV); the analyses show the presence of traces of gold compounds of higher carbon content which are difficult to separate.

cyclo*Pentamethylenemonobromogold* (V).—To an aqueous solution of compound (III), a slight excess of hydrobromic acid was added; the colourless crystalline precipitate obtained was extracted with ligroin (b. p. up to 40°), in which it was sparingly soluble but moderately stable at low temperatures. The ligroin solution was washed with water, dried with anhydrous sodium sulphate, and concentrated at the ordinary temperature under reduced pressure, the product crystallising in long colourless needles, which decomposed explosively at 80° [Found : Br, 23·3; Au, 56·9. $(C_5H_{10}BrAu)_2$ requires Br, 23·0; Au, 56·8%]. The instability of the compound, its behaviour in various solvents, and attempts to determine its molecular weight have been described above.

The cost of this investigation has been met from grants from Imperial Chemical Industries Limited and from the Government Grants Committee of the Royal Society. One of the authors (A. B.) gratefully acknowledges a maintenance grant from the Academic Assistance Council.

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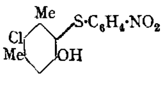
73. o-*Nitrophenylsulphenates of Phenols.*

By ERIC K. LEARMONTH and SAMUEL SMILES.

THE products obtained from the fusion of 2-nitrophenylchlorothiol with ψ-cumenol or 2-chloro-*m*-5-xylenol were provisionally regarded (J., **1934**, 424) as the sulphenates of these phenols (*e.g.*, II). This view has now been found to be incorrect; the substances are evidently hydroxy-sulphides (*e.g.*, I), since they yield acetyl derivatives and are different from the sulphenates which have been obtained from the sodium salts of these phenols and 2-nitrophenylchlorothiol. These and other sulphenates of similar type under suitable conditions are converted by hydrogen chloride into the hydroxy-sulphides (*e.g.*, II ⟶ I). The 2-nitrophenylsulphenate of *m*-5-xylenol yielded a sulphide to which the structure (III) must be assigned, since the corresponding sulphone did not show the characteristic rearrangement of *o*-hydroxy-sulphones in alkaline media. The formation of this *p*-hydroxy-sulphide suggests that the conversion of sulphenates of phenols into hydroxy-sulphides is not a true intramolecular rearrangement. The conclusion is supported by the fact that in molten phenol the sulphenate (II) and hydrogen chloride yielded the sulphide (IV). The 2-nitrophenylsulphenates of the more fully substituted phenols are more stable than that derived from phenol (compare Zincke, *Annalen*, 1912, **391**, 71), but they are destroyed by hydrogen peroxide in acetic acid and are slowly hydrolysed in alkaline media.



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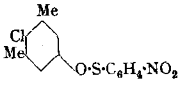

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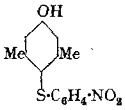

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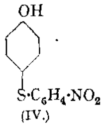

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EXPERIMENTAL.

The 2-nitrophenylsulphenates of the phenols were obtained by slowly adding a concentrated solution of the sodium phenoxide in alcohol to a cooled stirred solution of 2-nitrophenylchlorothiol (1 mol.) in ether. The insoluble product was washed with water to remove sodium chloride and the residue was usually purified by addition of water to a cold acetone solution. The yellow crystalline sulphenates obtained in most cases began to decompose at about 120°. They were destroyed by hydrogen peroxide or other oxidising agents in warm acetic acid, the formation of the corresponding sulphonates not being observed; they were hydrolysed with varying ease by warm aqueous sodium hydroxide (2*N*). Their behaviour with hydrogen chloride is described below.

2-Nitrophenylsulphenate of	M. p.	N, % found.	N, % calc.	2-Nitrophenylsulphenate of	M. p.	N, % found.	N, % calc.
1 *m*-4-Xylenol	85°	5·1	5·1	4 2 : 6-Dichloro-*m*-5-xylenol	125—127°	4·0	4·1
2 *m*-5-Xylenol	74	5·1	5·1	5 5-Chloro-*p*-2-xylenol	120	4·4	4·5
3 2-Chloro-*m*-5-xylenol	118—120	4·4	4·5	6 *ψ*-Cumenol	103	4·8	4·8

Conversion of the sulphenates into the hydroxy-sulphides was effected by leading hydrogen chloride into boiling benzene solutions; the process was usually complete in 30 minutes, and sometimes, *e.g.*, in Nos. 1 and 2, required only 10 minutes. After removal of benzene and hydrogen chloride the residue was purified from a suitable solvent. The following sulphides were obtained in this manner. 2-Nitro-2'-hydroxy-3' : 5'-dimethyldiphenyl sulphide, from No. 1, had m. p. 120° (Found : N, 5·0. Calc. : N, 5·1%) and was identical with the sulphide previously obtained (J., 1934, 422) from *m*-4-xylenol and the chlorothiol at 110°. The *methyl* ether formed pale yellow needles from alcohol, m. p. 79° (Found : N, 4·7. $C_{15}H_{15}O_3NS$ requires N, 4·8%).

2-*Nitro*-4'-*hydroxy*-2' : 6'-*dimethyldiphenyl sulphide* (III) was obtained (*a*) from No. 2 with hydrogen chloride or (*b*) from the interaction of *m*-5-xylenol and the chlorothiol at 80—100°. It formed yellow needles, m. p. 154°, from benzene (Found : C, 61·0; H, 4·7; N, 5·0. $C_{14}H_{13}O_3NS$ requires C, 61·1; H, 4·7; N, 5·1%). The *acetyl* derivative, pale yellow needles from alcohol, had m. p. 121° (Found : N, 4·4. $C_{16}H_{15}O_4NS$ requires N, 4·4%); and the *methyl* ether, m. p. 130°, formed yellow prisms from alcohol (Found : N, 4·7. $C_{15}H_{15}O_3NS$ requires N, 4·8%). In contrast with the sulphides obtained from Nos. 3 and 6 the sodium salt of this sulphide was readily formed from and soluble in aqueous alkali hydroxide (2*N*).

2-*Nitro*-4'-*hydroxy*-2' : 6'-*dimethyldiphenylsulphone* was obtained from the sulphide (4 g.) by oxidation (3 hours) in acetic acid (20 c.c., 100°) with hydrogen peroxide (7·3 c.c., 30%); it formed cream-coloured needles, m. p. 218° (decomp.), from acetic acid (Found : C, 54·4; H, 4·3; N, 4·4. $C_{14}H_{13}O_5NS$ requires C, 54·7; H, 4·2; N, 4·5%). This sulphone was recovered from a solution in aqueous alkali hydroxide (2*N*) which had been warmed and kept (2 hours); the contrast of this behaviour with that of analogous *o*-hydroxy-sulphones is evident (compare J., 1934, 422).

3'-Chloro-2-nitro-6'-hydroxy-2' : 4'-dimethyldiphenyl sulphide (I) was obtained (*a*) from No. 3 with hydrogen chloride in benzene or (*b*) from 2-chloro-*m*-5-xylenol and the chlorothiol as previously described (J., 1934, 424); it formed yellow needles from acetic acid, m. p. 196° (Found : N, 4·5. Calc. : N, 4·5%). The *acetyl* derivative formed pale yellow needles, m. p. 145°, from alcohol (Found : C, 54·4; H, 3·9. $C_{16}H_{14}O_4NClS$ requires C, 54·6; H, 4·0%). The orange sodium salt of this sulphide is sparingly soluble in aqueous alkali hydroxide and is readily hydrolysed; it was obtained by shaking a benzene solution of the sulphide with the alkaline reagent. The *methyl* ether, obtained by boiling (5 hours) a solution of the sodium salt in benzene containing methyl iodide and a little methyl alcohol, formed yellow prisms, m. p. 156°, from acetic acid (Found : C, 55·9; H, 4·2; N, 4·3. $C_{15}H_{14}O_3NClS$ requires C, 55·6; H, 4·3; N, 4·3%).

Conversion of the sulphenate No. 3 into the hydroxy-sulphide (IV) was effected as follows : Hydrogen chloride was led into a solution of the sulphenate (10 g.) in phenol (60 g.). When reaction was complete (80°, 30 mins.) the phenols were removed with steam and the finely powdered residue was shaken with excess of cold aqueous sodium hydroxide (2*N*). A small quantity of the sulphide (I) and its sodium salt remained insoluble; addition of dilute sulphuric acid to the solution yielded the sulphide (IV), which, after purification from benzene, had m. p. 130—131° and was identical with a sample prepared by Zincke's method (*loc. cit.*).

2-Nitro-2'-hydroxy-3' : 5' : 6'-trimethyldiphenyl sulphide was obtained (*a*) from No. 6 with hydrogen chloride in benzene or (*b*) from *ψ*-cumenol and 2-nitrophenylchlorothiol at 100—110° as already described (J., 1934, 424) (Found : N, 4·8. Calc. : N, 4·8%). Purified from acetone, it had m. p. 161°. The *acetyl* derivative formed yellow needles, m. p. 135°, from acetic acid (Found : C, 61·7; H, 5·0. $C_{17}H_{17}O_4NS$ requires C, 61·6; H, 5·1%). This hydroxy-sulphide is insoluble in aqueous alkali hydroxide (2*N*) and the formation of a sodium salt was not observed when a benzene solution was shaken with the reagent.

The conversion of the nitrophenylsulphenates into the hydroxy-sulphides serves in most cases as a convenient source of the latter substances, but the method is inapplicable in some cases where the phenol is highly substituted; *e.g.*, the sulphenate No. 4 under the usual treatment yielded the phenol and 2-nitrophenylchlorothiol.

KING'S COLLEGE, LONDON. [*Received, January 14th, 1936.*]

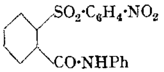
74. *A Rearrangement of Carbamyl-sulphones and -sulphides.*

By Wilfrid J. Evans and Samuel Smiles.

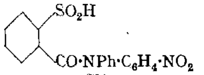
The conversion of 2'-nitro-2-acetamidodiphenylsulphone into nitroacetyldiphenylamine-2-sulphinic acid by alkaline media (J., 1935, 181) suggests that the *anilide* (I) should behave in a similar manner, since it provides the intramolecular conditions which promote this type of rearrangement (*loc. cit.*). The formation of 2-nitro-*N*-acetyldiphenylamine from (I) by reaction with alkali hydroxide shows that the expected rearrangement may be effected; evidently the sulphinic acid (II) at first formed suffers hydrolysis during the latter stages of the process. Similarly the m-*nitroanilide* of 2-nitrophenylsulphonylacetic acid (I, $C_6H_4{\cdot}NO_2$ instead of Ph) yielded 2 : 3'-dinitrodiphenylamine. With the homologous *sulphone* (III), evidence of rearrangement could not be obtained, 2-nitrobenzenesulphinic acid being the only product containing the nitrophenyl nucleus isolated after reaction with alkali. A similar result was obtained with the corresponding *sulphide*. In these cases the suppression of the intramolecular displacement observed with the sulphide corresponding to (I) may be attributed to the less favourable steric relations

(I.)	(II.)	(III.)
$CH_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2$ / $CO{\cdot}NHPh$	$CH_2{\cdot}SO_2H$ / $CO{\cdot}NPh{\cdot}C_6H_4{\cdot}NO_2$	$H_2C<$ $CH_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2$ / $CO{\cdot}NHPh$

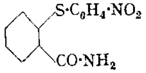
between the positive carbon of the nitrophenyl nucleus and the amido-nitrogen; the products arising from the tendency (Nicolet, *J. Amer. Chem. Soc.*, 1931, **53**, 3066) of β-thio-derivatives of propionic acid to suffer cleavage at the sulphur group thus predominate. The sulphonyl group of the *anilide* (IV) is less easily removed by hydrolysis than that of (III); in this case rearrangement proceeded readily, yielding the sulphinic acid (V), which after methylation was identified by hydrolysis, the products being 2-methylsulphonylbenzoic acid and 2-nitrodiphenylamine. Also the *sulphide* corresponding to (IV) gave with warm alkali hydroxide a thiol (V, SH instead of SO_2H), which after methylation and oxidation yielded the methylsulphone derived from (V). The *o*-nitroanilide of 2-thiolbenzoic acid was obtained from the amide (VI) by rearrangement and was characterised by the *methyl* ether, which was also synthesised. This behaviour of the amide (VI) contrasts with the inactivity of 2'-nitro-2-aminodiphenyl sulphide (VI, NH_2 instead of $CO{\cdot}NH_2$) under similar conditions and accords with the results of previous experiments (J., 1935, 183) which showed that acylation of the amino-group with an acid of moderate strength favours the rearrangement.



(IV.)



(V.)

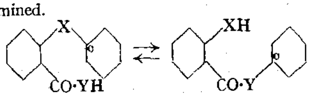


(VI.)

Further consideration of the intramolecular conditions (*loc. cit.*) governing the process shows that the influence of acylation on less active groups than amino which serve as YH (VIII, *loc. cit.*, p. 182) may have an adverse influence. This may occur when YH is hydroxyl; *e.g.*, whereas derivatives of 2'-nitro-2-hydroxydiphenylsulphone (IV, OH instead of CO·NHPh) are converted (J., 1934, 422) into sulphinic acids by cold alkali hydroxide, the 2'-nitrodiphenylsulphone-2-carboxylic acid (IV, CO_2H instead of CO·NHPh) is unattacked under these conditions.

The rearrangement of the sulphone (IV), that of the sulphide (VI) and of their derivatives now described forecasts the interconversion of systems such as (VII) and (VIII), which contain suitable intramolecular conditions (compare J., 1935, 184). Some of these systems are being examined.

(VII.)



(VIII.)

Experimental.

2-*Nitrophenylthioacetanilide*.—The acid (21 g.) (Claasz, *Ber.*, 1912, **45**, 747) was dissolved in excess of warm thionyl chloride (55 c.c.), the latter removed by evaporation under diminished pressure, the oily chloride dissolved in acetone (65 c.c.), and the solution treated with excess of aniline in presence of sodium bicarbonate. The *anilide* was isolated by admixture with dilute hydrochloric acid and crystallised from alcohol; m. p. 159—160° (Found: C, 58·2; H, 4·6; N, 9·6. $C_{14}H_{12}O_3N_2S$ requires C, 58·3; H, 4·2; N, 9·7%).

2-*Nitrophenylsulphonylacetanilide* (I) was obtained from the sulphide (3·1 g.) by oxidation (1·5 hours) with "hyperol" (5·2 g.) in acetic acid (30 c.c.; 100°). The product, isolated in the usual manner and purified from alcohol, had m. p. 151—152° (Found: C, 58·2; N, 8·8; S, 9·8. $C_{14}H_{12}O_5N_2S$ requires C, 52·5; N, 8·8; S, 10·0%). Rearrangement of this sulphone (1·0 g.) in boiling alcohol (10 c.c.) was rapidly (5 mins.) effected by the addition of *N*-sodium hydroxide (1 mol.). The solution then contained a mixture of 2-nitro-*N*-acetyldiphenylamine and the sulphinic acid (II); hydrolysis of the latter was completed by addition of more *N*-sodium hydroxide (1 mol.) and further heating (10 mins.). 2-Nitro-*N*-acetyldiphenylamine (0·5 g.) separated when the solution was cooled; after purification it had m. p. 133—134° (Found: N, 11·1. Calc.: N, 10·9%) and was converted into 2-nitrodiphenylamine by hydrolysis with 60% sulphuric acid.

2-*Nitrophenylthioaceto*-m-*nitroanilide* was obtained by boiling (20 mins. a solution of the chloride of the acid (10 g.) and *m*-nitroaniline (14 g.) in benzene. It was purified from acetic acid and had m. p. 216—217° (Found: N, 12·6. $C_{14}H_{11}O_5N_3S$ requires N, 12·6%).

2-*Nitrophenylsulphonylaceto*-m-*nitroanilide*.—Acetic acid (100 c.c.) containing the sulphide (6·6 g.) and hydrogen peroxide (10 c.c., 30%) was heated (100°), after 30 minutes more hydrogen peroxide (5 c.c.) was added, then (15 mins.) the solution was cooled and the product, which separated, was purified from acetic acid; it had m. p. 207° (Found: C, 46·2; N, 11·4; S, 8·9. $C_{14}H_{11}O_7N_3S$ requires C, 46·0; N, 11·5; S, 8·8%). After a suspension of this sulphone (1·0 g.) in *N*-sodium hydroxide (10 c.c.) had been boiled for a few minutes, 2 : 3'-dinitrodiphenylamine (0·6 g.) separated; this had m. p. 159° and was identified by comparison with a synthetic specimen (Evans and Smiles, J., 1935, 187).

2-*Nitrophenylthioacetamide* was obtained (82%) by interaction of ammonia and the chloride in benzene solution; it had m. p. 178—179° (Found: N, 13·1. $C_8H_8O_3N_2S$ requires N, 13·2%).

2-*Nitrophenylsulphonylacetamide*, obtained from the sulphide by oxidation with hydrogen peroxide in the usual manner, was purified from alcohol and had m. p. 155—156° (Found: C, 39·4; N, 11·7; S, 13·1. $C_8H_8O_5N_2S$ requires C, 39·3; N, 11·5; S, 13·1%). For comparison with the behaviour of the corresponding anilide which has been recorded it is worth notice that after a solution of this sulphone (1·0 g.) in *N*-sodium hydroxide (1·25 mols.) had been boiled (1 hour), a part (0·25 g.) was recovered, the only products observed being those arising from hydrolysis.

β-2-*Nitrophenylthiopropionic Acid* (compare III).—An aqueous solution of the sodium salts of β-chloropropionic acid and 2-nitrophenylthiol was boiled (1·5 hour), then cooled, and acidified with dilute sulphuric acid. The product contained 2-nitrophenylthiol, which was removed by conversion into the disulphide; the *acid* was then purified from alcohol, it had m. p. 147° (Found: C, 47·4; H, 4·1. $C_9H_9O_4NS$ requires C, 47·6; H, 4·0%). The *anilide* obtained from this acid as in the case of the acetic acid derivative had m. p. 166° after purification from acetic acid (Found: C, 59·8; H, 4·9; N, 9·1. $C_{15}H_{14}O_3N_2S$ requires C, 59·6; H, 4·6; N, 9·2%).

β-2-*Nitrophenylsulphonylpropionanilide* (III) separated (7·2 g.) from the cooled reaction mixture which had been obtained by oxidising (30 mins.) the corresponding sulphide (10 g.) with hydrogen peroxide (16·4 c.c., 30%) in hot acetic acid (100 c.c.). After purification from alcohol it had m. p. 186—187° (Found: N, 8·2; S, 9·5. $C_{15}H_{14}O_5N_2S$ requires N, 8·4; S, 9·6%). Treatment of this sulphone and of the sulphide in hot alcohol with aqueous sodium hydroxide yielded 2-nitrobenzenesulphinic acid and 2-nitrophenylthiol respectively, which were each identified by methylation and by conversion into the disulphide.

Derivatives of o-*Thiolbenzoic Acid*.—(1) 2-o-*Nitrophenylthiobenzamide* (VI). A mixture of *o*-nitrophenylthiobenzoic acid (20 g.) and thionyl chloride (40 c.c.) was warmed (below 60°) until solution of the former was complete. The crystalline acid chloride which remained after the excess of thionyl chloride had been removed was converted into the *amide* by reaction with ammonia in benzene (15—20°). The product was purified (80%) from alcohol and then had

m. p. 164° (Found: C, 56·7; H, 4·0; S, 11·4. $C_{13}H_{10}O_3N_2S$ requires C, 56·9; H, 3·7; S, 11·7%).

(2) 2-o-*Nitrophenylthiobenzanilide*, obtained from the acid chloride by reaction with excess of warm aniline, had m. p. 127—128° (Found: C, 64·8; H, 4·3; N, 7·9. $C_{19}H_{14}O_3N_2S$ requires C, 65·1; H, 4·0; N, 8·0%).

The sulphones were obtained from the sulphides (1) and (2) by oxidation (100°) with excess of hydrogen peroxide (4 mols.; 30%) in acetic acid. Purified from alcohol, 2-o-*nitrobenzenesulphonylbenzamide* (3) had m. p. 193—194° (Found: C, 51·2; S, 10·4. $C_{13}H_{10}O_5N_2S$ requires C, 51·0; S, 10·5%), and 2-o-*nitrobenzenesulphonylbenzanilide* (IV) (4) had m. p. 184° (Found: C, 59·8; N, 7·2; S, 8·4. $C_{19}H_{14}O_5N_2S$ requires C, 59·7; N, 7·3; S, 8·4%).

Rearrangements.—A solution of the sulphide (1) (1·0 g.) in alcohol (10 c.c.) containing sodium hydroxide (*N*/2, 1·25 mols.) was boiled (40 mins.). When it was cooled, a small quantity of the sulphide (I) separated; this was removed and methyl iodide was added to the solution, which was again boiled (10 mins.). The 2-*methylthiobenzo-o-nitroanilide* crystallised (0·22 g.) from the reacting mixture; after purification from alcohol it had m. p. 111° and was identified by comparison with the product synthesised from the interaction of *o*-nitroaniline and 2-methylthiobenzoyl chloride in benzene (Found: C, 58·0; H, 4·4. $C_{14}H_{12}O_3N_2S$ requires C, 58·3; H, 4·1%).

When the sulphone (3) (2 g.) was suspended in boiling *N*-sodium hydroxide (1·25 mols.), it soon (10 mins.) dissolved. 2-*Methylsulphonylbenzo-o-nitroanilide* separated when the product of this rearrangement was methylated; it had m. p. 221° and was identical with the material obtained by oxidising the above methylthiol with hydrogen peroxide in acetic acid (Found: C, 52·6; N, 8·6; S, 10·2. $C_{14}H_{12}O_5N_2S$ requires C, 52·5; N, 8·7; S, 10·0%).

Rearrangement of the sulphone (4) (2 g.) was easily (5 mins.) effected by boiling *N*-sodium hydroxide (1·25 mols.). The product present in the deep red solution was isolated after methylation (1·9 g.). Thus obtained, 2-*methylsulphonylbenzo-2'-nitrodiphenylamide* (compare V) was purified from acetic acid and had m. p. 206° (Found: C, 60·4; N, 7·1; S, 8·0. $C_{20}H_{16}O_5N_2S$ requires C, 60·6; N, 7·1; S, 8·1%). It was identified by hydrolysis (2 hours) with hot alcoholic sodium hydroxide. When the solution then obtained had been cooled and diluted, 2-nitrodiphenylamine separated; acidification of the filtrate yielded 2-methylsulphonylbenzoic acid. These products were identified in the usual manner.

Rearrangement of the sulphide (2) took place when it (4 g.) was kept (15 mins.) in boiling alcohol (35 c.c.) containing 0·5*N*-sodium hydroxide (1·25 mols.). Methyl iodide was then added and methylation was assisted by further boiling (15 mins.). After the excess of methyl iodide had been removed, the product separated from the cooled mixture (2·7 g.); after being purified from alcohol, it had m. p. 145—146° and was identified as 2-*methylthiobenzo-2'-nitrodiphenylamide* (Found: C, 66·3; H, 4·6; N, 7·7. $C_{20}H_{16}O_3N_2S$ requires C, 65·9; H, 4·4; N, 7·7%) by oxidation, which yielded the above sulphone obtained by rearrangement of sulphone (4).

King's College, London. [*Received, January 14th*, 1936.]

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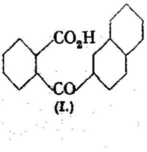
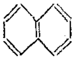
75. *Remarks on the Structure of Naphthalene.*

By Ernst Bergmann and Jehuda Hirshberg.

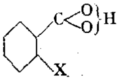
In spite of all the available information regarding the structure of the naphthalene system, we have neither definite knowledge nor even very exact data. One of the most striking features is the fact that a 2-hydroxy- or 2-amino-naphthalene couples with diazo-compounds exclusively in the 1- and not in the 3-position; *i.e.*, with regard to a 2-position, the 1- but not the 3-position behaves like an *o*-position. Furthermore, cyclisation of a suitable β-substituted naphthalene, *e.g.*, (I), usually involves the α-position, although the competitive cyclisation may be effected under different conditions.



(I.)



(II.



(III.)

(1) The first phenomenon has never been tested quantitatively. The present communication deals with the dissociation constants of *o*-chlorinated naphthoic acids: we obtained the following data for p_K, the measurements being carried out in acetone–water (1 : 1) as solvent for reasons of solubility.

Acid.	p_K.	Acid.	p_K.
1-Naphthoic	4·80	2-Naphthoic	4·67
2-Chloro-1-naphthoic	3·90	1-Chloro-2-naphthoic	3·80
8-Chloro-1-naphthoic	4·05	3-Chloro-2-naphthoic	4·37

The first conclusion to be drawn from these data is that the influence of a chlorine atom in the 1-position on the constant of the 2-naphthoic acid is the same as that of a 2-chlorine atom on the 1-naphthoic acid: the ratio between the respective constants is nearly the same (1·23) for both pairs. On the other hand, the chlorine atom in position 3 has a much smaller influence on the 2-naphthoic acid, which confirms the more qualitative assumption of organic chemists.

It is not easy to explain these results in terms of the theory of aromatic nuclei; it may be that the naphthalene system is not aromatic in the benzenoid sense. If we assume that in benzene there is no real difference between the various linkages of the nucleus, we may conclude that in naphthalene there are double and single bonds in the purely aliphatic sense, and that they have a fixed position and do not undergo any rearrangement. The further necessary assumption that an influence of the observed type is transmissible only through a double, not through a single, bond leads to a formula like (II) for naphthalene. [The validity of that assumption may be based on the consideration that in the system (III) two single bonds lie between the polar halogen bond (C–X) and the place of the dissociation: the transmission of polar effects through such systems of linkages has been treated theoretically by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668).] The same conclusion has been reached by Fieser and Lothrop (*J. Amer. Chem. Soc.*, **1935**, **57**, 1459; cf. quinoline, Le Fèvre, J., 1935, 1470). According to the wave-mechanical treatment of the naphthalene molecule (Sherman, *J. Chem. Physics*, 1934, **2**, 488; cf. Kohlrausch, *Ber.*, 1935, **68**, 893), the above structure makes a considerably greater contribution to the wave function than any of the other possible structures (compare also Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2708).

According to that hypothesis, the influence concerned is not due to " steric hindrance," but is a merely " inductive effect "; any effect transmitted outside the nucleus should be the same for the 1 : 2- and the 2 : 3-position. Then, the influence of the 8-chlorine atom on the dissociation constant of 1-naphthoic acid, which is nearly as great as when it is in the 2-position, should be a really steric one, since no effect should be transmitted along the path from the 1- to the 8-position (3 single bonds).

(2) Similar conclusions may be drawn from dipole data. For 1 : 8-disubstituted naphthalenes, the following data were obtained:

	μ.	μ'.		μ.	μ'.
1-*Chloro*-8-*fluoronaphthalene*	2·86	3·01	1-Chloro-8-iodonaphthalene	2·55	2·86
1 : 8-Dichloronaphthalene	2·78	3·12	1 : 8-Dinitronaphthalene	7·87	7·96
1-Chloro-8-bromonaphthalene	2·64	3·05			

Since theoretically the moment of these naphthalene derivatives is equal to the sum (μ') of the substituent moments (the moment values used for F, Cl, Br, I, NO_2 are 1·45, 1·56, 1·49, 1·30, 3·96 respectively), the data give immediately a measure of the respective influences. If it is assumed that the difference between μ and μ' is due to a real valency deflexion, the angle between the halogen valencies is nearly proportional to the atomic radii of the halogens (96 : 114 : 120 : 120), but that consideration has only a formal value, and it would be interesting to determine the places of the halogen atoms by the method of electronic diffraction (for *o*-di-iodobenzene, see Hendricks, Maxwell, Mosley, and Jefferson, *J. Chem. Physics*, 1933, **1**, 549; cf. Schopp and Wolf, *Chem. Zentr.*, 1935, II, 2040).

The dipole moment of 1 : 8-dinitronaphthalene is nearly equal to the theoretical value —the small deviation may be due to experimental errors, since the compound is very sparingly soluble. The reason for this striking result may be that the nitro-groups do not

lie in the plane of the nucleus, but in a perpendicular one, so that the steric disturbance is very small. Solvent effects, which may always invalidate discussion of dipole moments, will not greatly affect the above conclusions.

(3) The speed of alkaline hydrolysis of the methyl chloronaphthoates may also give a qualitative clue to the structural features of the naphthalene system. The measurements were carried out in methyl alcohol as solvent, and time was recorded in minutes:

Methyl 1-naphthoate	$k_{60^\circ} = 0{\cdot}0206$	Methyl 1-*chloro-2-naphthoate*	$k_{62^\circ} = 0{\cdot}0354$
,, 2-chloro-1-naphthoate	$k_{60^\circ} = 0$ *	,, 3-chloro-2-naphthoate	$k_{63^\circ} = 0{\cdot}068_7$
,, 8-*chloro-1-naphthoate*	$k_{80^\circ} = 0$	,, benzoate †	$k_{60^\circ} = 0{\cdot}049_0$
,, 2-naphthoate	$k_{59^\circ} = 0{\cdot}0153$	,, *o*-chlorobenzoate ‡	$k_{61^\circ} = 0{\cdot}036_8$

* The stability of this ester towards hydrol ysis and the lability of the 3-chloro-isomeride were recorded by Meyer (*Ber.*, 1895, **28**, 182).

† Cf. Treu, Diss., Hamburg, 1926.

‡ Studied by Kellas (*Z. physikal. Chem.*, 1897, **24**, 243) under similar conditions.

The absolute magnitude of the constants for methyl 1- and 2-naphthoates cannot readily be explained; for the α-compound, the depression with regard to the methyl benzoate constant may be due to the *o*-position being blocked by the second nucleus (cf. methyl *o*-chlorobenzoate), but the still lower value for the β-isomeride cannot be accounted for. The case is complicated by the fact that chlorination of methyl 2-naphthoate in the 1- and especially in the 3-position raises the hydrolysis constant. Such a rise would be expected only for the 3-chlorinated ester by analogy with methyl chloroacetate and acetate (cf. Freudenberg, "Stereochemie," 1932, p. 485) or similar pairs; that view would support the naphthalene formula discussed above.

That the 2-chlorination of methyl 1-naphthoate makes the resulting ester inaccessible to the hydrolytic agent, may be explained by the double ortho-substitution; but the behaviour of the 8-chloro-derivative is inexplicable, since the introduction of the chlorine atom merely enlarges the size of the ortho-substituent (the second nucleus) already present. It is obvious that we are dealing with a specific relation between the 1 : 8-substituents, and, in contrast to the p_K data, the hydrolysis data are not amenable to mathematical analysis, owing to the overlapping of various factors (8-*chloro-1-naphthonitrile* has an abnormally high dipole moment, 5·70, instead of the maximum theoretical value 5·47, which shows that 1 : 8-naphthalene derivatives are anomalous).

Experimental.

Materials.—1-Naphthoic acid and 1 : 8-dinitronaphthalene were commercial samples, recrystallised from dilute acetic acid and pyridine, respectively; m. p.'s 161°, 171°. 2-Naphthoic acid was prepared according to Salkind (*Ber.*, 1934, **67**, 1031), m. p. 182°; and 2-chloro-1-naphthoic acid according to Rabe (*Ber.*, 1889, **22**, 394), m. p. 151—152° from benzene (yield 27%).

3-*Chloro-2-naphthoic acid.* Commercial 3-amino-2-naphthoic acid (68 g.) was converted into the hydrochloride by heating with concentrated hydrochloric acid (300 c.c.), diazotised with sodium nitrite (27 g.), and slowly poured into a cold solution of cuprous chloride (copper filings, 180 g.; copper chloride, 20 g.; concentrated hydrochloric acid, 80 c.c.; water, 20 c.c.). The precipitate was purified by dissolving it in sodium carbonate solution and acidifying (yield, nearly quantitative); m. p. 212—213° (Hosaeus, *Ber.*, 1893, **26**, 668, gives 216°) from benzene. Esterification (*Ber.*, 1901, **34**, 4161) by heating with ethyl alcohol in a stream of hydrogen chloride proceeded normally; b. p. 195—197°/18 mm., from light petroleum, m. p. 57—59° (Found: C, 66·3; H, 4·7. $C_{13}H_{11}O_2Cl$ requires C, 66·7; H, 4·7%).

1-*Chloro-2-naphthoic acid.* 1-Hydroxy-2-naphthoic acid was converted into 1-chloro-2-naphthoyl chloride by means of phosphorus pentachloride (Strohbach, *Ber.*, 1901, **34**, 4161). The chloro-chloride was treated for 3 hours with its own weight of boiling methyl alcohol, and the resnlting crude ester (b. p. 189—193°/17·5 mm.) was hydrolysed by boiling 15% methyl-alcoholic potassium hydroxide. The potassium salt was dissolved in warm water, and the solution acidified, the acid forming white needles, m. p. 195° (yield, 46%) from 50% acetic acid (Wolffenstein, *Ber.*, 1888, **21**, 1190, gives 196°).

8-Chloro-1-naphthoic acid was prepared from its nitrile (see below) by conversion into the amide and hydrolysis of the latter (Kalb, *Ber.*, 1914, **47**, 1726). It was obtained as an oil, crystallising on standing, and was recrystallised from benzene; yellowish crystals, m. p. 169—170° (Kalb gives 167°).

1-Chloro-8-fluoronaphthalene. 8-Chloro-1-naphthylamine (30 g.) was diazotised in concentrated hydrochloric acid (41·5 c.c.) with sodium nitrite (13 g.), and the filtered solution mixed with borofluoric acid (140 c.c.; 40%); the precipitated *diazonium borofluoride* had m. p. 106—107° (decomp.) (yield, 32 g.; 80%) (Found, by the method of Wilke-Dörfurt and Balz, *Ber.*, 1927, **60**, 116: N, 10·3. $C_{10}H_6N_2ClF_4B$ requires N, 10·4%). Thermal decomposition gave 1-*chloro-8-fluoronaphthalene* in 50% yield; b. p. 130—132°/12·5 mm., m. p. 44° (Found: C, 66·8; H, 3·5. $C_{10}H_6ClF$ requires C, 66·5; H, 3·3%).

1 : 8-*Dichloronaphthalene.* The diazo-solution prepared as above was introduced slowly into a boiling solution of cuprous chloride (copper sulphate, 125 g.; water, 250 c.c.; sodium chloride, 60 g.; copper turnings, 65 g.; concentrated hydrochloric acid, 500 c.c.), and the product isolated by steam distillation; m. p. 84—85° from alcohol (Altenberg, *Ber.*, 1876, **9**, 1732, gives 83°); yield, 17·5 g. (52%).

1-*Chloro-8-bromonaphthalene.* 8-Chloro-1-naphthylamine (52 g.) was dissolved in a solution of cuprous bromide (copper sulphate, 35 g.; potassium bromide, 116 g.; copper filings, 30 g.; concentrated sulphuric acid, 19 c.c.; water, 300 c.c.) and diazotised with sodium nitrite (22 g.). Extraction with ether and distillation in a vacuum gave the desired product, which was purified from light petroleum; m. p. 94—95°; yield 7 g. (17%) (I. G. Farbenind. give m. p. 87—88°; see *Chem. Zentr.*, 1930, II, 1466). Guareschi and Biginelli's compound of m. p. 119—119·5° (*Gazzetta*, 1887, **16**, 152) cannot be this 1-chloro-8-bromo-compound, but may be the otherwise unknown 1 : 5-derivative.

1-*Chloro-8-iodonaphthalene.* To the diazo-solution prepared as for the corresponding fluoro-compound, 50 g. of potassium iodide were added slowly. The mixture was heated on the water-bath for 1 hour, the brown precipitate dissolved in ether, the solution shaken with sodium thiosulphate, and the ether evaporated. Distillation in a vacuum (b. p. 197—198°/19 mm.) and recrystallisation from alcohol gave the pure product; m. p. 79—80°; yield 14 g. (28%) (0·1804 g. gave 0·2376 g. of AgCl + AgI. Calc. for $C_{10}H_6ClI$: 0·2365 g. AgCl + AgI) (compare Vieth, *Annalen*, 1875, **180**, 319).

8-*Chloro-1-naphthonitrile.* The diazo-solution prepared as above was mixed with a solution of 42·5 g. of potassium cuprocyanide. After 12 hours, the mixture was heated for 2 hours on the water-bath, the product isolated by suction, dried, and distilled in a vacuum; b. p. 242—244°/15·5 mm. Repeated crystallisation from alcohol gave silky needles, m. p. 145—146°; yield, 22% (Found: C, 70·5; H, 3·2. $C_{11}H_6NCl$ requires C, 70·6; H, 3·2%).

Methyl 1-naphthoate was obtained in quantitative yield from 1-naphthoic acid (10 g.) and methyl alcohol (200 c.c.) by heating for 2 hours in a stream of hydrogen chloride; b. p. 165°/17 mm. (Found: C, 77·2; H, 5·7. Calc.: C, 77·4; H, 5·4%). Methyl 2-naphthoate, prepared in the same way, was recrystallised from methyl alcohol; m. p. 76°. Methyl 2-chloro-1-naphthoate was prepared from the acid by means of ethereal diazomethane solution. The distilled ester (b. p. 176—180°/18·5 mm.) crystallised immediately and, after trituration with light petroleum, had m. p. 50° (Rabe, *Ber.*, 1889, **22**, 394).

Methyl 8-chloro-1-naphthoate was prepared in the same way (5 g. acid, 1 g. diazomethane); b. p. 188—189°/16·2 mm. (Found: C, 65·2; H, 4·2. $C_{12}H_9O_2Cl$ requires C, 65·4; H, 4·1%); and the 1-*chloro-2-naphthoate*, similarly prepared, afforded white needles, m. p. 48—49° (Found: Cl, 16·3. $C_{12}H_9O_2Cl$ requires Cl, 16·1%), from light petroleum.

Methyl 3-chloro-2-naphthoate. This was obtained by use of diazomethane, and also from 3-chloro-2-naphthoyl chloride (Strohbach, *Ber.*, 1901, **34**, 4159) by reaction with 5 times its weight of methyl alcohol. It crystallised spontaneously on evaporation and was purified from methyl alcohol; m. p. 58—59° (Ullmann, *Ber.*, 1918, **51**, 22, gives 58°).

Methyl *o*-chlorobenzoate, prepared according to Kellas (*loc. cit.*), had b. p. 119·5—120·5°/24·4 mm.

Measurements.—The dissociation constants of the halogenated naphthoic acids were determined by the method of " half-titration " from electrometrical titrations, the Cambridge Potentiometer apparatus and glass electrodes being used. The dipole measurements were carried out in benzene solution by the methods adopted in our laboratory (Bergmann, Engel, and Sándor, *Z. physikal. Chem.*, 1930, *B*, **10**, 113, where the significance of the symbols in the following tables is explained). The refractive indices were determined with the Zeiss interferometer.

The hydrolysis of the esters was effected by means of methyl-alcoholic potassium hydroxide solution. The ester was weighed into a 100-c.c. measuring flask, the equivalent amount of the hydroxide solution added from a burette, then most of the methyl alcohol, and the mixture was kept in the thermostat for 5 minutes and then diluted to the mark. After definite time intervals,

f.	$\bar{M}$.	ρ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
				1-*Chloro-8-fluoronaphthalene*; t = 19·4°.					
0	78	0·8794	2·2852	2·2852	26·603	26·603	—	—	→
0·00994	79·018	0·8857	2·4077	2·2927	28·493	26·866	216·90	53·15	163·75
0·01221	79·252	0·8872	2·4343	2·2943	28·894	26·924	214·25	52·91	161·34
0·01458	79·494	0·8887	2·4634	2·2954	29·328	26·978	213·60	52·93	161·67
0·01931	79·979	0·8917	2·5157	2·2999	30·107	27·115	208·07	53·14	155·93
				P^{∞}_{A+O} = 172·0; μ = 2·86 D.					
				1 : 8-*Dichloronaphthalene*; t = 14·5°.					
0	78	0·8851	2·2951	2·2951	26·449	26·449	—	—	→
0·01109	79·319	0·8941	2·4318	2·3060	28·660	26·906	225·94	67·68	158·25
0·01324	79·575	0·8959	2·4610	2·3082	29·090	26·971	226·76	65·95	160·81
0·01525	78·814	0·8975	2·4778	2·3105	29·348	27·036	216·65	65·00	151·65
0·03923	82·669	0·9270	2·7708	2·3299	33·102	27·391	196·03	(50·48)	145·58
				P^{∞}_{A+O} = 166·0; μ = 2·78 D.					
				1-*Chloro-8-bromonaphthalene*; t = 13·5°.					
0	78	0·8863	2·2972	2·2972	26·566	26·566	—	—	→
0·00692	79·130	0·8947	2·3802	2·3045	27·869	26·805	215·07	61·14	153·93
0·00944	79·543	0·8962	2·4081	2·3075	28·353	26·943	215·90	66·49	149·41
0·01318	80·153	0·9001	2·4581	2·3118	29·126	27·092	220·87	66·50	154·37
0·01622	80·650	0·9032	2·4912	2·3154	29·647	27·217	216·60	66·73	149·87
				P^{∞}_{A+O} = 157·5; μ = 2·64 D.					
				1-*Chloro-8-iodonaphthalene*; t = 13·6°.					
0	78	0·8862	2·2970	2·2970	26·566	26·566	—	—	→
0·00603	79·268	0·8963	2·3629	2·3052	27·628	26·813	202·63	67·42	135·21
0·00875	79·841	0·9009	2·3912	2·3092	28·079	26·926	199·42	67·71	131·71
0·01194	80·513	0·9062	2·4293	2·3139	28·670	27·061	202·71	68·01	134·70
0·01465	81·083	0·9071	2·4546	2·3180	29·187	27·284	205·46	75·54	120·92
				P^{∞}_{A+O} = 140·0; μ = 2·55 D.					
				8-*Chloro-1-naphthonitrile*; t = 18·8°.					
0	78	0·8801	2·2864	2·2864	26·599	26·599	—	—	→
0·00292	78·320	0·8816	2·4274	2·2895	28·640	26·705	727·6	64·8	662·8
0·00423	78·463	0·8821	2·4780	2·2909	29·350	26·753	677·7	64·3	613·4
0·00599	78·656	0·8833	2·5583	2·2928	30·442	26·817	669·6	63·9	605·7
0·00808	78·885	0·8844	2·6481	2·2950	31·626	26·894	649·4	63·8	585·6
				P^{∞}_{A+O} = 687·0; μ = 5·70 D.					
				1 : 8-*Dinitronaphthalene*; t = 14·1°.					
0	78	0·8857	2·2962	2·2962	26·569	26·569	—	—	→
0·00053	78·074	0·8860	2·3400	2·2964	27·207	26·589	1236·57	64·53	1172·04
0·00074	78·103	0·8861	2·3553	2·2968	27·492	26·602	1193·17	61·62	1131·55
0·00099	78·175	0·8862	2·3702	2·2970	27·657	26·626	1122·47	83·18	1039·29
0·00151	78·212	0·8865	2·3894	2·2976	27·926	26·700	922·33	(112·80)	809·53
				P^{∞}_{A+O} = 1330·0; μ = 7·87 D.					

10 c.c. were run into ice-cold water and titrated with 0·1N-hydrochloric acid. In the following tables t is the time in minutes, a the initial concentration of alkali and ester in c.c. of 0·1N-acid per 100 c.c., and a—x their concentration (in the same units) at time t. The velocity constants, therefore, are given by the equation $k = 100x/at(a - x)$.

Methyl α-naphthoate.

0·4966 G. of ester; a = 26·81; 60°.

t.	$a - x$.	k.	t.	$a - x$.	k.
11·5	26·6	0·0256	48·5	26·2	0·0179
23·0	26·4	0·0252	58·5	26·1	0·0173
33·0	26·3	0·0219	74·5	26·0	0·0156
					k = 0·0206

Methyl β-naphthoate.

0·5158 G. of ester; a = 27·79; 59°.

t.	$a - x$.	k.	t.	$a - x$.	k.
46	27·0	0·0231	137	26·2	0·0161
76	27·0	0·0140	178	26·2	0·0098
108	26·6	0·0150	239	25·5	0·0136
					k = 0·0153

Methyl 1-chloro-2-naphthoate.

0·5645 G. of ester; a = 25·60; 62°.

t.	$a - x$.	k.	t.	$a - x$.	k.
31	25·0	0·0225	202	21·2	0·0299
78	23·1	0·0404	347	18·9	0·0297
111	22·5	0·0361	498	15·1	0·0406
138	21·7	0·0379	1343	8·2	0·0459
					k = 0·0354

Methyl 3-chloro-2-naphthoate.

0·5551 G. of ester; a = 25·17; 63°.

t.	$a - x$.	k.	t.	$a - x$.	k.
30	22·7	0·1073	201	17·5	0·0645
73	21·4	0·0714	343	16·5	0·0453
103	20·2	0·0706	489	12·2	0·0643
136	19·1	0·0691	1338	7·0	0·0574
					k = 0·0687

Methyl o-*chlorobenzoate.* 0·5579 G. of ester; a = 32·86; 61°.

t.	$a - x$.	k.	t.	$a - x$.	k.	t.	$a - x$.	k.	t.	$a - x$.	k.
18·5	31·6	0·0656	37·0	31·4	0·0383	57·5	31·1	0·0300	81·5	30·5	0·0289
28·5	31·5	0·0372	46·0	31·2	0·0352	70·5	30·6	0·0319	95·0	30·3	0·0271
											k = 0·0368

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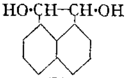
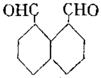
76. *The Preparation of Acenaphthylene Glycol and Some Condensation Reactions of Naphthalene*-1 : 8-*dialdehyde.*

By B. K. Blount and A. Weissberger.

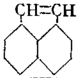
Criegee, Kraft, and Rank (*Annalen*, 1933, **507**, 159) have shown that acenaphthylene glycol (I) is oxidised by lead tetra-acetate to naphthalene-1 : 8-dialdehyde (II). The usefulness of this reaction depends on the availability of the glycol, hitherto obtainable only from the difficultly accessible acenaphthylene (III). A more promising source appeared to be acenaphthenequinone (IV). The first product of its reduction would undoubtedly be a benzoin, and in the experience of one of us further reduction would only take place satisfactorily in absence of oxygen (*J. pr. Chem.*, 1930, **127**, 260), since in alkaline solution benzoins autoxidise very rapidly (J., 1935, 226).



(I.)



(II.)



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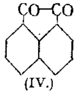
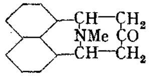


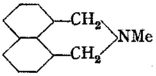
(IV.)

We have accordingly reduced acenaphthenequinone by means of sodium amalgam and alcohol in an atmosphere of nitrogen, and have isolated *cis*-acenaphthylene glycol in some 35% yield. The reduction of phenanthraquinone, carried out in the same way, proceeds only as far as 9 : 10-dihydroxyphenanthrene. The reason for this difference is evidently that 9 : 10-dihydroxyphenanthrene is a true aromatic *o*-dihydroxy-compound, whereas the corresponding reduction product of acenaphthenequinone (the enolic form of the α-ketol) is not.

Oxidation of *cis*-acenaphthylene glycol proceeds as described by Criegee *et al.*, giving naphthalene-1 : 8-dialdehyde. Neither this aldehyde nor 1 : 8-diacetylnaphthalene condenses with *o*-diamines or 1 : 8-diaminonaphthalene to give substances of the quinoxaline type.

Positive results were, however, obtained in the tropinone condensation. Using Robinson's conditions (J., 1932, 1429), we finally obtained 1-methyl-2 : 6(1′ : 8′)-naphthapiperid-4-one (V) isolated as the *picrate*, together with the *picrate* of a base $C_{13}H_{13}N$. The latter compound presumably originates from the condensation of the aldehyde and methylamine, with simultaneous reduction, and is probably (VI). When the condensation was carried out in buffered solution at p_H 6·5 (cf. Schöpf and Lehmann, *Annalen*, 1935, **518**, 1), the tropinone alone was formed.

(V.)




(VI.)

Experimental.

cis-*Acenaphthylene Glycol* (I).—The reduction was carried out in a round-bottomed flask provided with an efficient mercury-sealed stirrer, a tap funnel, and a source of oxygen-free nitrogen. A liquid seal was provided for the escape of the gas. Acenaphthenequinone (5·5 g.) and 3% sodium amalgam (250 g.) were placed in the flask, and the air completely replaced by

nitrogen. Absolute alcohol (200 c.c.) was added through the tap funnel, the flask placed in a water-bath at 50°, and the mixture stirred. The solution soon became dark blue, and much blue solid separated. This gradually dissolved, and none remained after 24 hours' stirring; the colour of the solution was still blue, though less intense. Glacial acetic acid (20 c.c.) and water (50 c.c.) were then added through the tap funnel, causing the solution to become orange. (In the remaining stages of the preparation access of air is not prejudicial.) The mercury was separated, and the alcoholic solution clarified from a trace of amorphous material by filtering through charcoal. From the filtrate, four fractions (all melting above 160°) were obtained by addition of water and evaporation of alcohol. They were recrystallised from benzene (charcoal) and finally from aqueous alcohol, giving 1·5—2 g. of pure *cis*-acenaphthylene glycol. The mother-liquors gave a lower-melting mixture of both isomerides.

1-Methyl-2 : 6(1' : 8')-naphthapiperid-4-one (V).—The crude aldehyde prepared by the oxidation of acenaphthylene glycol (360 mg.) was condensed with acetonedicarboxylic acid (1 g.), chalk (1·4 g.), and 33% aqueous methylamine (4 c.c.) in methyl alcohol-water (1 : 1; 25 c.c.). After 24 hours the solution was acidified and boiled, the calcium precipitated as oxalate, and the bases extracted with ether. The brown oily mixture of bases was converted by means of picric acid in acetone into the picrates (378 mg.). These were separated by repeated crystallisation from acetone into a less soluble component [thin yellow plates, m. p. 197° (decomp.)] and a more soluble component (large, compact, garnet-red crystals, m. p. 165—166°). The yellow substance, m. p. 197°, was *1-methyl-2 : 6(1' : 8')-naphthapiperid-4-one picrate* (Found : C, 56·3, 57·0; H, 4·1, 4·1; N, 12·2. $C_{22}H_{18}O_8N_4$ requires C, 56·7; H, 3·9; N, 12·0%). The free base could not be crystallised, and failed to give a characteristic dipiperonylidene derivative (cf. Blount, J., 1933, 553). The red substance, m. p. 165—166°, gave the analytical figures required for the *picrate* of a base $C_{13}H_{13}N$ (Found : C, 55·5; H, 3·9; N, 13·8. $C_{19}H_{16}O_7N_4$ requires C, 55·3; H, 3·9; N, 13·6%).

When the aldehyde (*M*/1000), acetonedicarboxylic acid (*M*/500), and methylamine (*M*/500) in 50% alcohol (50 c.c.), buffered with phosphate to p_H 6·5, were allowed to react for 5 days at 22°, the tropinone was formed exclusively, but the yield (15 mg. of the picrate) was not good.

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The Dyson Perrins Laboratory, Oxford. [*Received, December 6th*, 1935.]

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77. *Chlorination of Toluene in Presence of* (a) *Activated Charcoals and* (b) *Iron-impregnated Silica Gel. Production of Side-chain Substitution, Nuclear Substitution, and Tolan Derivatives.*

By James B. Firth and Trevor A. Smith.

The chlorination of boiling toluene in the dark and in presence of catalysts has been investigated. Two types of catalyst were used : (*a*) activated and impregnated charcoal, (*b*) silica gels containing a small amount of iron.

From the results obtained (see table), the presence of activated sugar charcoal accelerates the formation and increases the yield of side-chain substitution products. The activity in this respect appears to be slightly increased by previous sorption of iodine. With blood charcoal, the catalytic effect is much greater, the chlorination of the side chain being practically complete after 8 hours (No. 6); and chlorination for 16 hours gives rise to *2 : 2'-dichlorotolan dichloride*. The formation of this compound is probably due to the chlorination of benzotrichloride to *o*-chlorobenzotrichloride, which under the influence of the catalyst condenses to form 2 : 2'-dichlorotolan tetrachloride; this on distillation decomposes with the formation of dichlorotolan dichloride.

The activity of the catalyst deteriorates on "activating" at higher temperatures. The introduction of iron into sugar carbon does not materially affect the catalytic activity.

Iron-impregnated silica gel induces nuclear substitution. It also induces condensation, with the result that, when the time of chlorination exceeds about 3 hours, the product includes tarry matter, the amount increasing with the duration of chlorination.

In the experiments with iron-impregnated silica gel as catalyst, glue-like products were obtained, probably owing to condensation of simpler chlorination products. In order to test this view the action of the catalyst alone on benzyl chloride was tried; after a lag of 2—3 minutes a violent reaction occurred, and dense clouds of hydrogen chloride were evolved. The reaction appeared to be complete in about 1 minute. The product was a reddish-brown glue with a blue fluorescence. The reaction was brought under control by dissolving the benzyl chloride in half its weight of light petroleum. The glue-like product was soluble in petroleum, acetone, benzene, and chloroform, all the solutions being highly fluorescent; but from them and many other solvents tried, a glue invariably resulted; no crystalline product could be obtained.

EXPERIMENTAL.

Preparation of Catalysts.—Series (a). *Sugar charcoal* was prepared by carbonising cane sugar, the resulting carbon being finely ground, washed with hot water, and dried at 100°.

Iodised sugar charcoal. Sugar charcoal was treated with *N*/10-iodine in chloroform for 24 hours, separated by filtration, gently warmed to remove most of the iodine, washed with alcoholic caustic potash and then with water, and dried at 100° (cf. Firth and Watson, J., 1923, **123**, 1219).

Blood charcoal. " Mercks " blood charcoal, which contained 0·24% of iron, was used.

" *Artificial* " *blood charcoal* was prepared by adding a solution of ferrous oxalate to a concentrated solution of cane sugar, followed by excess of aqueous ammonia; the liquid was evaporated to dryness and the residue was carbonised at as low a temperature as possible, washed with water, and dried at 100°.

Series (b). *Silica gel impregnated with iron.* 20 G. of ferric chloride were dissolved in 100 c.c. of hydrochloric acid (*d* 1·140) and 100 c.c. of sodium silicate solution (*d* 1·156) were slowly added with vigorous stirring to prevent local precipitation. In about ½ hour, the mixed solutions set to a firm clear gel. This was broken up and dried on a water-bath; sodium chloride which crystallised on the surface was removed from time to time by washing with water, this treatment being continued until there was no appreciable separation of salt (about 3 days). The product was thoroughly washed, dried by gradual heating to 200°, ground, again washed, and dried at 200°. The activity of the catalyst was liable to vary over quite a wide range, and in order to obtain concordant results the above procedure should be carried out as quickly as possible. The activity of the catalyst was considerably diminished (1) when the preliminary removal of sodium chloride was carried out by rapid heating to a relatively high temperature, and (2) after several days' storage. The average iron content of the final gel was 3·5 ± 0·5%. The portion of catalyst to be used in an experiment was activated by heating in a vacuum at the required temperature.

Chlorination.—Toluene was chlorinated in the dark at its boiling point in presence of a known weight of catalyst for a definite period. The weight, volume, and density of the product were determined. It was then steam-distilled; in some experiments, benzoic acid separated. The dried distillate was fractionated several times; the fraction collecting up to 180° was weighed, and its density determined. This fraction contained unchanged toluene, *o*- and *p*-chlorotoluenes, benzyl chloride, and, in some experiments, benzaldehyde. The benzyl chloride was determined by boiling a known weight of the distillate with alcohol and solid silver nitrate and weighing the silver chloride produced (cf. Silberrad, Silberrad, and Parke, J., 1925, **127**, 1726). The other constituents were determined by the method of Cohen, Dawson, Blockley, and Woodmansey (J., 1910, **97**, 1623).

In some experiments benzylidene chloride was a product (benzaldehyde obtained on steam-distillation). In these experiments the steam distillate was divided into two fractions, (*a*) up to 120° (unchanged toluene), (*b*) 120—185° (chlorinated products). The composition of (*b*) was determined as before, the density of benzaldehyde being substituted for that of toluene in the formula. A summary of typical results is set forth in the following tables.

The dark-coloured, neutral, high-boiling product obtained in experiment 10 probably contained cis- and trans-2 : 2′-*dichlorotolan dichloride*, since on fractional distillation and recrystallisation from acetone, the fraction, b. p. *ca.* 220°/30 mm., yielded about 7 g. of yellow crystalline substance. The first crop had m. p. 170°, and the last m. p. 139°. The different crops gave similar analytical results and were therefore probably isomeric forms of the same substance (Found: C, 53·4; H, 2·5; Cl, 43·4. $C_{14}H_8Cl_4$ require C, 52·8; H, 2·5; Cl, 44·7%). Boiling with pyridine furnished a compound (yellow needles) having the m. p. of 2 : 2′-dichlorotolan.

Series (*a*). Activated Charcoals. 100 G. of Toluene in each Experiment.

No.	Catalyst and temp. of activation.	Hours of chlorination.	Fractionated product. W., g.	d.	Benzyl chloride, %.	Chlorotoluenes, %.	Toluene, %.	Benzaldehyde, %.	Benzoic acid, g.
1	Nil	8	76	1·050	42	37	21	—	—
2	1 G. sugar charcoal, 600°	8	82	1·087	73	24	3	—	—
3	1 G. sugar charcoal, iodised, 600°	8	87	1·085	90	8	2	—	—
4	1 G. sugar charcoal, 900°	8	61	1·082	89	5	6	—	—
5	1 G. sugar charcoal, iodised, 900°	8	80·5	1·081	88·5	4·5	7	—	—
6	Blood charcoal, 600°	8	—	—	—	—	—	—	126
7	,, ,,	4	9·0	1·068	87	3	8	2	nil
8	,, ,, 800°	8	35·5	1·077	30	7	7	56	32
9	,, ,, 900°	8	70	1·074	68	22	10	—	nil
10	,, ,, 600°	16	—	—	—	—	—	—	33
11	Artificial blood charcoal, 600°	8	98	1·086	81	11	8	—	nil

Series (*b*). Iron-impregnated Silica Gel. 100 G. of Toluene in each Experiment.

1	1 G., 600° for 2 hours	4	64	0·998	trace	63	37
2	1 G., 120° for 12 hours	4	64	1·053	nil	89	11
3	1 G., 600° for 2 hours	8	49	1·035	19·5	61	19·5
4	2 G., 600° for 2 hours	8	(Crude product, black brittle solid)				

In series (*b*), a brown glue remained after steam-distillation, the amount being greater in experiment 3 than in 1 and 2. This glue, distilled under 12·15 mm., gave a pale yellow fraction, b. p. 210—220°. Chlorine was given off and a carbonaceous residue remained. The distillate became semi-solid on cooling, and on recrystallisation from alcohol–acetone (1 : 3) deposited yellow crystals, m. p. 145° [Found : (i) C, 67·2; H, 4·1; Cl, 28·4; (ii) C, 67·6; H, 4·0; Cl, 28·5. $C_{14}H_{10}Cl_2$ requires C, 67·5; H, 4·0; Cl, 28·5%] (cf. Onufrowicz, *Ber.*, 1884, **17**, 883).

Experiment 4 [series (*b*)]. Repeated extraction with acetone yielded a glue, from which *no pure crystalline product could be isolated. Another portion, distilled at 2 mm., gave off* chlorine, leaving a carbonaceous residue. A few drops of yellow liquid distilled at 300—340°, which set to a hard glue. Several solvents were tried, but no pure crystalline product could be obtained. To reduce glue formation, experiment 3 [series (*b*)] was repeated, the time of chlorination being reduced to 3 hours. The product on distillation yielded a fraction, b. p. 230—260°, from which a white solid deposited on cooling; recrystallised from acetone, this gave needles, m. p. 82°, b. p. 230°/715 mm. On boiling with alcoholic silver nitrate, no turbidity was produced, showing the absence of side-chain substitution products [Found : (i) C, 43·0; H, 2·1; Cl, 54·9; (ii) C, 42·85; H, 2·6; Cl, 54·55. Calc. for $C_7H_5Cl_3$: C, 43·0; H, 2·6; Cl, 54·5%].

In three experiments in which portions of the same catalyst material were used (*a*) as soon as possible after preparation, (*b*) after 14 days, (*c*) after 28 days, the yields of this product were 38 g., 28 g., and 14·5 g., respectively. From the above data it was concluded that the product was probably 2 : 4 : 5-trichlorotoluene (cf. Seelig, *Annalen*, 1897, **237**, 129).

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78. *Studies on Hydrogen Cyanide. Part VII. Aldehydes from Aromatic Hydrocarbons.*

By L. E. Hinkel, E. E. Ayling, and J. H. Beynon.

It was shown by Hinkel, Ayling, and Morgan (J., 1932, 2793) that Gattermann's hydrogen cyanide aldehyde synthesis, thitherto regarded as inapplicable to aromatic hydrocarbons (Houben and Fischer, *J. pr. Chem.*, 1929, **123**, 319; Wieland and Dorrer, *Ber.*, 1930, **63**, 404), could, by variation of the reaction temperature, be applied to benzene for the synthesis

of benzaldehyde (Brit. Pat., 397,124, 1933), contrary to the observations of Gattermann, who used benzene as a solvent in the synthesis. The reaction was extended to other liquid hydrocarbons, such as toluene and the xylenes, and in each case an excess of the hydrocarbon was used as a solvent in the reaction. This method, however, has its limitations and can only be used in those cases where the hydrocarbon is liquid, easily procurable and, furthermore, unaffected by the presence of the free aluminium chloride which has been shown to be necessary in the reaction.

The applicability of the process for the complete conversion of hydrocarbons into the corresponding aldehydes by means of an excess of hydrogen cyanide and aluminium chloride in the presence of suitable solvents has now been studied.

Tetrachloroethane, *o*-dichlorobenzene, and chlorobenzene can be used as reaction media in the preparation of resorcylaldehyde (this vol., p. 184). These liquids are also particularly suitable for the aluminium chloride reactions, since they serve as solvents not only for the hydrocarbons but also for the hydrogen cyanide and the final products, and their relatively high boiling points render possible a study of the reaction over a wide range of temperature. In addition, none of them is affected by aluminium chloride or gives rise to the Friedel–Crafts reaction under the conditions used, although chlorobenzene can be made to yield *p*-chlorobenzaldehyde in small amount under special conditions.

The choice of solvent is a matter of importance, since the solvent appears to exert a marked influence on the reaction, depending on its chlorine content. Tetrachloroethane, with its high chlorine content, appears to enhance the aldehyde synthesis with most hydrocarbons, but on the other hand it also considerably increases the tendency for the polymerisation or condeusation of those hydrocarbons which are prone to these reactions iu the presence of aluminium chloride (compare Scholl and Seer, *Ber.*, 1922, **55**, 109, 330; Scholl and Neumann, *ibid.*, p. 118; Scholl and Schwarzer, *ibid.*, p. 324; Schaarschmidt, Mayer-Bugström, and Sevon, *Ber.*, 1925, **58**, 156; Homer, J., 1907, **91**, 1103; Wieland and Dorrer, *Ber.*, 1930, **63**, 404). The latter tendency is usually preferential to, and in some cases completely inhibits, the aldehyde synthesis, as, for example, with indene. In these cases, the polymerisation may be prevented to a large extent by using a solvent with a lower chlorine content, such as chlorobenzene, and also by using a smaller excess of aluminium chloride with a longer duration of the reaction period.

The union of hydrogen chloride with the compound $AlCl_3,2HCN$, although inappreciable at the ordinary temperature, is fairly rapid at 80° and the resulting compound $AlCl_3(HCN)_2HCl$ readily dissociates at 100° (J., 1935, 674). The choice of the reaction temperature in the aldehyde synthesis is thus governed by two opposing factors, since, though the rate of formation of arylmethyleneformamidine hydrochloride, R·CH:N·CH:NH,HCl, increases with rise in temperature, the tendency for the aluminium chloride to cause polymerisation and nuclear condensation is also increased. For most cases the results obtained indicate 70° as the approximate optimum reaction temperature. It may be stated as a broad generalisation that, when the hydrocarbon is not readily acted upon by aluminium chloride, one molecule of free aluminium chloride is necessary for optimum conversion of the hydrocarbon into aldehyde. When the reactivity of the hydrocarbon is great, the necessary concentration of free aluminium chloride must be reduced and the reaction period increased accordingly.

Chloromethyleneformamidine reacts with benzene in the presence of aluminium chloride to yield benzaldehyde (Hinkel and Dunn, J., 1930, 1836), and this reaction has now been extended to the following hydrocarbons: acenaphthene, anthracene, diphenyl, hydrindene, and naphthalene. It was hoped that in some cases it might be possible to prepare dialdehydes, since some hydrocarbons readily yield diketones in the Friedel–Crafts reaction (compare Dziewonski and Schnayder, *Bull. intern. acad. polonaise*, 1930, *A*, 529; Dziewonski and Spirer, *ibid.*, 1931, *A*, 232). In all cases, however, with the exception of diphenyl, only the monoaldehydes are obtained, identical with those prepared by the hydrogen cyanide method.

Diphenyl, besides being the only hydrocarbon examined with which a dialdehyde could be formed, presents a case with some novel features. The formation of this dialdehyde proceeds in an unusual manner, both the aldehyde groups being introduced simultaneously,

since under no conditions can the monoaldehyde be converted into the dialdehyde. In each reaction with diphenyl, the product is always either diphenyl-4-aldehyde and unchanged diphenyl or, on the other hand, when disubstitution occurs, diphenyl-4 : 4'-dialdehyde and unchanged diphenyl, a mixture of the two aldehydes never being obtained. In this reaction the solvent exerts a marked influence. With chlorobenzene or *o*-dichlorobenzene, the product consists of the monoaldehyde, but with tetrachloroethane, only the dialdehyde results.

The following new aldehydes have been isolated : *acenaphthene-3-aldehyde*, *anthracene-9-aldehyde*, 1 : 6-*dimethyl-4-naphthaldehyde*, 2 : 6-*dimethyl-1-naphthaldehyde*, and *fluorene-2-aldehyde*. An anthracene-9-aldehyde has been previously prepared, but no proof of its constitution has been given (I. G. Farbenind. A.-G. and Carpmael, Brit. Pat., 311,208, 1928; *Brit. Chem. Abs.*, 1929, *B*, 747). The aldehyde now synthesised is quantitatively oxidised to 9 : 10-anthraquinone and the aldehyde group must therefore be in the 9-position. Oxidation of acenaphthenealdehyde yielded naphthalene-1 : 4 : 5-tricarboxylic acid, and the two dimethylnaphthaldehydes similarly yielded 1 : 6-dimethyl-4- and 2 : 6-dimethyl-1-naphthoic acids respectively, thereby establishing the constitutions of these compounds.

Braun and Engel (*Ber.*, 1924, **57**, 191) describe a fluorene-2-aldehyde, m. p. 174—175°; semicarbazone, m. p. 245—247°, which they prepared from 2-cyanofluorene through 2-fluorenylmethyl bromide by the method of Sommelet (*Compt. rend.*, 1913, **157**, 852). The fluorenealdehyde obtained by the hydrogen cyanide method differs considerably, however, from that of Braun and Engel, since it melts at 90° and yields a semicarbazone, m. p. 278°. On oxidation it yields fluorene-2-carboxylic acid and fluorenone-2-carboxylic acid, both of which are identical with the acids obtained from 2-cyanofluorene by the method of Fortner (*Monatsh.*, 1904, **25**, 451). Similarly the fluorenone-2-carboxylic acid, obtained either by oxidation of the fluorenealdehyde or from 2-cyanofluorene, yields the authentic diphenyl-2 : 4'-dicarboxylic acid when fused with potash (compare Kruber, *Ber.*, 1932, **65**, 1382). The constitution of the aldehyde is further established by its conversion into 2-methylfluorene (Kruber, *Ber.*, 1932, **65**, 1382).

Since 2-nitrofluorene (Diels, *Ber.*, 1901, **34**, 1758) was used both by Braun and Engel and by Fortner for the production of 2-cyanofluorene, there can be no doubt that the fluorenealdehyde now obtained by the hydrogen cyanide method is fluorene-2-aldehyde. It therefore seems that Braun and Engel could not have obtained a pure aldehyde by their method. An attempt to convert 2-cyanofluorene directly into fluorene-2-aldehyde by the method of Stephen (J., 1925, **127**, 1874) was unsuccessful, 2-cyanofluorene being quantitatively recovered.

Experimental.

Apparatus and Materials.—The apparatus was similar to that described by Hinkel, Ayling, and Morgan (*loc. cit.*). The hydrogen chloride was dried by means of phosphoric oxide, and anhydrous hydrogen cyanide was obtained by fractionation of the commercial material, followed by drying with phosphoric oxide and refractionation. Commercial tetrachloroethane, chlorobenzene, and *o*-dichlorobenzene, supplied by Imperial Chemical Industries, Ltd., were dried over calcium chloride, and fractionally distilled. Benzene was purified by sulphuric acid, dried over calcium chloride, followed by sodium, and distilled. Aluminium chloride was obtained from Imperial Chemical Industries, Ltd., and other chemicals were purchased as pure materials.

General Procedure for the Preparation of Aldehydes.—Powdered aluminium chloride was suspended in the solvent and hydrogen cyanide was added slowly during 15 minutes through the dropping-funnel, the reaction vessel being shaken and cooled in ice-water. The mixture, in which the solid increased in bulk owing to the formation of the double compound $AlCl_3,2HCN$ as a white crystalline powder, was kept at room temperature for 15 minutes with frequent shaking in order to complete the union of the aluminium chloride with the hydrogen cyanide. The requisite hydrocarbon was then added, and a slow current of hydrogen chloride passed through the mixture for 15 minutes at room temperature. The mixture was then heated in a water-bath for the period and temperature specified (reaction period and temperature), the passage of dry hydrogen chloride through the mixture, which was well shaken at 10-minute intervals, being maintained throughout. The dark viscous product was poured on ice and

concentrated hydrochloric acid, and the mixture boiled for 15 minutes. The aldehydic product was then isolated as described in each particular instance.

As the above procedure was used in each case, only the quantities of materials, the temperature, and the reaction period are given in the individual cases; furthermore, the experimental details refer only to those experiments in which the optimum yield of aldehyde was obtained. The yields of aldehydes are calculated on the chloromethyleneformamidine basis and expressed in terms of the hydrocarbon.

Chlorobenzene.—This was subjected to the reaction in order to test its suitability as a solvent. Chlorobenzene (112 g., 10 mols.), hydrogen cyanide (16 c.c., 4 mols.), and aluminium chloride (53 g., 4 mols.) were subjected to the general procedure for 6 hours at 100°. Yield : 2·2 g., 8% (calc. on the HCN). The decomposed reaction mixture was distilled in steam, and the aldehydic distillate extracted with ether. The extract was shaken for 8 hours with saturated aqueous sodium bisulphite, and the bisulphite compound and solution decomposed by boiling for 5 minutes with *N*-sulphuric acid. The liberated *p*-chlorobenzaldehyde was isolated by distillation in steam, extraction in ether, and fractionation in colourless needles, m. p. 45°, b. p. 212—214°.

Mesitylene.—Mesitylene (14 c.c., 1 mol.), tetrachloroethane (100 c.c.), hydrogen cyanide (24 c.c., 6 mols.), aluminium chloride (53·4 g., 4 mols.); time, 4 hours at 80°. Yield : 12·3 g., 83%. From the resulting reaction mixture, 2 : 4 : 6-trimethylbenzaldehyde, b. p. 236—237°, was isolated according to the procedure described by Hinkel, Ayling, and Morgan (*loc. cit.*).

When the proportion of aluminium chloride was increased from 4 to 5 mols., with the other quantities and conditions as given above, the yield of aldehyde was diminished to 67%.

Ethylbenzene.—Ethylbenzene (21·2 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (32 c.c., 4 mols.), aluminium chloride (66·8 g., 2·5 mols.); time, 4 hours at 100°. Yield : (liquid, b. p. 224—228°), 6 g., 22·4%. The decomposed reaction mixture was distilled in steam, the aldehydic distillate extracted with ether, the extract shaken for 8 hours with excess of saturated aqueous sodium bisulphite, and the bisulphite solution removed, acidified with excess of 4*N*-sulphuric acid, and distilled in steam. The dried ethereal extract of this aldehydic distillate, on fractionation, yielded a mixture, b. p. 215—260°. Further distillation yielded no definitely pure fraction, although *p*-ethylbenzaldehyde (b. p. 221°) was proved to be present in the fraction, b. p. 224—228°, by means of its semicarbazone (compare Fournier, *Compt. rend.*, 1903, **136**, 558; Hinkel, Ayling, and Morgan, *loc. cit.*).

With tetrachloroethane (100 c.c.) *as solvent, the yield of liquid* (b. p. 224—228°) *was* only 15%.

Diphenyl.—Diphenyl (15·4 g., 1 mol.), tetrachloroethane (100 c.c.), hydrogen cyanide (12 c.c., 3 mols.), aluminium chloride (33·4 g., 2·5 mols.); time, 7 hours at 75°. Yield : 13·6 g., 75%. The resulting diphenyl-4-aldehyde was isolated from the decomposed reaction mixture according to the procedure described by Hey (J., 1931, 2476). It crystallised from light petroleum (b. p. 80—100°) in very pale yellow laminae, m. p. 60°, and was further identified by means of its phenylhydrazone, m. p. 188—189° (compare Gattermann, *Annalen*, 1906, **347**, 381), and its 2 : 4-dinitrophenylhydrazone, m. p. 239° (compare Hey, *loc. cit.*).

Naphthalene.—Naphthalene (25·6 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 3 mols.), aluminium chloride (66·8 g., 2·5 mols.); time, 5 hours at 70°. Yield : 18·7 g., 60%. The decomposed reaction product was steam-distilled, and the aldehydic distillate extracted with ether. The α-naphthaldehyde was isolated by means of its sodium bisulphite compound in the nsual way and obtained as a pale yellow oil, b. p. 291—292°, identified by means of its oxime, m. p. 98° (compare Brandis, *Ber.*, 1889, **22**, 2151).

The optimum temperature of 70° is shown by the results of three experiments, identical save for reaction temperature, which yielded aldehyde as follows : 50°, 31%; 70°, 52%; 80°, 32·5%.

1-*Methylnaphthalene.*—1-Methylnaphthalene (21·5 c.c., 1 mol.), *o*-dichlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 4 mols.), aluminium chloride (60 g., 3 mols.); time, 5 hours at 75°. Yield : 12·9 g., 51%. The resulting 1-methyl-4-naphthaldehyde was isolated according to the procedure described for ethylbenzene as a pale yellow oil, b. p. 171°/11 mm., and identified by means of its semicarbazone, which crystallised from alcohol in colourless plates, m. p. 229° (compare Ziegler and Tiemann, *Ber.*, 1922, **55**, 3416, and Robinson and Thomson, J., 1932, 2015, who record m. p. 228° and 237° respectively).

1 : 6-*Dimethylnaphthalene.*—1 : 6-Dimethylnaphthalene (31·2 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 3 mols.), aluminium chloride (66·8 g., 2·5 mols.); time, 5 hours at 70°. Yield : 21·3 g., 58%. After removal of the solvent from the decomposed

reaction mixture by distillation in steam, the residual non-volatile oil was extracted with ether. The ethereal extract was shaken for 8 hours with excess of saturated aqueous sodium bisulphite, the light brown bisulphite compound removed and washed with ether, and the aldehyde liberated as an oil by boiling with a slight excess of *N*-sulphuric acid for 5 minutes. Fractionation of the dried ethereal extract of the oil yielded 1 : 6-*dimethyl*-4-*naphthaldehyde* as a pale yellow oil, b. p. 191·5°/16 mm. (Found : C, 84·7; H, 6·6. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%). The *oxime* crystallised from light petroleum (b. p. 80—100°) in colourless laminae, m. p. 123° (Found : N, 7·0. $C_{13}H_{13}ON$ requires N, 7·0%), the *semicarbazone* from aqueous alcohol in colourless laminae, m. p. 202° (Found : N, 17·4. $C_{14}H_{15}ON_3$ requires N, 17·5%), and the *phenylhydrazone* from light petroleum (b. p. 60—100°) in yellow warts, m. p. 110° (Found : N, 10·1. $C_{19}H_{18}N_2$ requires N, 10·2%).

Oxidation of 1 : 6-*Dimethyl*-4-*naphthaldehyde*.—(a) *With aqueous potassium permanganate*. The aldehyde (3·6 g.), suspended in water (100 c.c.), was heated at 100° with a solution of potassium permanganate (3 g.) in water (100 c.c.) until the colour disappeared. The filtered liquid, on acidification with concentrated hydrochloric acid, yielded a white precipitate, which was washed with water, dried, and crystallised from benzene, 1 : 6-dimethyl-4-naphthoic acid (1·0 g.) separating in colourless needles, m. p. 188—189° (Found : equiv., 200·6. Calc., 200) (compare Barnett and Cook, J., 1933, 22).

(b) *Aerial oxidation*. A current of air was drawn through the aldehyde (2·0 g.), maintained at 150°, for 2 hours. The resulting brown solid was extracted with dilute sodium hydroxide solution, and the alkaline solution washed with ether and acidified. Crystallisation of the resulting precipitate from benzene yielded the above 1 : 6-dimethyl-4-naphthoic acid (1·5 g.).

2 : 6-*Dimethylnaphthalene*.—2 : 6-Dimethylnaphthalene (19·5 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (15 c.c., 3 mols.), aluminium chloride (33·4 g., 2 mols.); time, 5 hours at 70°. Yield : 14·1 g., 60%. The aldehyde was isolated through its sodium bisulphite compound by a procedure similar to that described under 1 : 6-dimethylnaphthalene. Crystallisation from light petroleum (b. p. 40—60°) yielded 2 : 6-*dimethyl*-1-*naphthaldehyde* in colourless laminae, m. p. 57° (Found : C, 84·8; H, 6·6. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%). The *oxime* crystallised from light petroleum (b. p. 80—100°) in colourless laminae, m. p. 122—123° (Found : N, 7·0. $C_{13}H_{13}ON$ requires N, 7·0%), the *semicarbazone* from alcohol in colourless laminae, m. p. 214° (Found : N, 17·3. $C_{14}H_{15}ON_3$ requires N, 17·5%), the *phenylhydrazone* from aqueous alcohol in pale yellow laminae, m. p. 122° (Found : N, 10·1. $C_{19}H_{18}N_2$ requires N, 10·2%), and the *aniline* derivative from light petroleum (b. p. 40—60°) in yellow plates, m. p. 78° (Found : N, 5·4. $C_{19}H_{17}N$ requires N, 5·4%).

Oxidation of 2 : 6-*Dimethyl*-1-*naphthaldehyde*.—The aldehyde (1·2 g.), oxidised with potassium permanganate (1 g.) according to the procedure described for 1 : 6-dimethyl-4-naphthaldehyde, yielded 2 : 6-dimethyl-1-naphthoic acid (0·6 g.), which crystallised from benzene in colourless prisms, m. p. 170—171° (Found : equiv., 200. Calc., 200) (Baeyer and Villiger, *Ber.*, 1899, **32**, 2429, record m. p. 168—171°).

1 : 2 : 3 : 4-*Tetrahydronaphthalene* (*Tetralin*).—Tetralin (20 c.c., 1 mol.), tetrachloroethane (100 c.c.), hydrogen cyanide (24 c.c., 4 mols.), aluminium chloride (60 g., 3 mols.); time, 5 hours at 75°. Yield : 0·96 g., 4%. The resulting aldehyde was isolated according to the procedure described for ethylbenzene. Fractionation of the dried ethereal extract of the aldehydic distillate yielded 1 : 2 : 3 : 4-tetrahydro-6-naphthaldehyde as a colourless oil, b. p. 138°/14 mm., further identified by its semicarbazone, which separated from alcohol in colourless needles, m. p. 219° (compare Braun, Moldänke, Dirlam, and Gruber, *Ber.*, 1922, **55**, 1700, who also obtained a 4% yield of the aldehyde by the action of carbon monoxide and hydrogen chloride in the presence of aluminium chloride). The tetralin is mainly converted into a non-aldehydic resinous product, owing to its great reactivity towards aluminium chloride (compare Schroeter, *Ber.*, 1924, **57**, 1990).

Hydrindene.—Hydrindene (20 c.c., 1 mol., prepared according to the method of Krämer and Spilker, *Ber.*, 1890, **23**, 3276), tetrachloroethane (100 c.c.), hydrogen cyanide (20 c.c., 3 mols.), aluminium chloride (56 g., 2·5 mols.); time, 6 hours at 80°. Yield: 11 g., 45%. The decomposed reaction mixture was distilled in steam, and the aldehydic distillate extracted with ether. Fractionation of the dried ethereal extract yielded hydrindene-5-aldehyde, b. p. 255—257°, further identified by means of its aniline derivative, m. p. 85° (compare Gattermann, *Annalen*, 1906, **347**, 347). The remainder of the hydrindene was converted by the aluminium chloride into a brown, non-volatile, non-aldehydic, ether-insoluble solid (12 g.).

Indene was completely polymerised to a brown, non-aldehydic, nitrogen-free solid, insoluble in acids and alkalis, under the conditions of the aldehyde synthesis, even when all the aluminium

chloride was combined as the compound $AlCl_3,2HCN$. This agrees with the ready activity of unsaturated compounds with aluminium chloride (compare Wieland and Dorrer, *loc. cit.*).

Anthracene.—Anthracene (27·7 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 4 mols.), aluminium chloride (60 g., 3 mols.); time, 5 hours at 70°. Yield: 18·5 g., 60%. After removal of the solvent from the decomposed reaction mixture by distillation in steam, the dark brown solid was crushed, washed with water, and extracted with ether. Evaporation of the extract deposited *anthracene-9-aldehyde*, which crystallised from dilute acetic acid in long orange needles, m. p. 104—105° (Found: C, 87·2; H, 4·8. $C_{15}H_{10}O$ requires C, 87·4; H, 4·9%).

When solutions of the aldehyde in alcohol or ether were allowed to crystallise slowly in sunlight, the resulting solid melted over a wide range, mainly at 104°, but not completely until 115° (compare Brit. Pat. 311,208, 1928, where anthracene-9-aldehyde is described as orange needles, m. p. about 104°). On prolonged keeping in sunlight, the aldehyde, m. p. 104—105°, assumed an indistinct melting range and appeared to be partly transformed into a solid of much higher m. p., complete fusion not occurring until 135°. No separation into fractions having melting ranges other than 104—105° could, however, be obtained by fractional crystallisation from any of the common solvents.

Anthracene-9-aldehyde displays similarity with anthraquinone in the non-formation of a sodium bisulphite compound at the ordinary temperature. It readily yields, however, the following derivatives by the usual methods: the *aniline* derivative crystallised from alcohol in orange needles, m. p. 175° (Found: N, 4·9. $C_{21}H_{15}N$ requires N, 5·0%), the *phenylhydrazone* from alcohol in orange needles, m. p. 207° (Found: N, 9·4. $C_{21}H_{16}N_2$ requires N, 9·5%), the *oxime* from alcohol in pale yellow laminae, m. p. 186—187° (Found: N, 6·25. $C_{15}H_{11}ON$ requires N, 6·3%), and the *semicarbazone* from alcohol in bright yellow, microscopic laminae, m. p. 291° (Found: N, 16·1. $C_{16}H_{13}ON_3$ requires N, 16·0%).

Oxidation of Anthracene-9-aldehyde.—Chromic acid (30 g.) in glacial acetic acid (20 c.c.) and water (20 c.c.) was added during 2 hours to the aldehyde (2 g.) in glacial acetic acid (30 c.c.) boiling under reflux, and the heating continued for a further 2 hours. Addition to water (1 l.) and crystallisation of the resulting white precipitate from aqueous acetic acid yielded anthraquinone (2 g.) in colourless needles, m. p. and mixed m. p. 281°.

Phenanthrene.—Phenanthrene (17·8 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (12 c.c., 3 mols.), aluminium chloride (26·7 g., 2 mols.); time, 5 hours at 50°. Yield: 9 g., 44%. The solvent was removed from the decomposed reaction mixture by distillation with steam, and the residual tarry aldehydic material extracted with ether. The filtered extract, shaken for 12 hours with excess of saturated aqueous sodium bisulphite, yielded a light brown solid, which was washed with ether and then decomposed by boiling for 5 minutes with excess of dilute sodium carbonate solution. The viscous oil formed was extracted with ether and fractionation of the extract yielded phenanthrene-9-aldehyde, b. p. 231—233°/12 mm., which solidified on cooling and crystallised from methyl alcohol in colourless needles, m. p. 100—101°; its oxime crystallised from aqueous alcohol in colourless plates, m. p. 157° (compare Mossetig and van de Kamp, *J. Amer. Chem. Soc.*, 1933, **55**, 2995).

Phenanthrene is readily polymerised by aluminium chloride (compare Scholl and Schwarzer; Schaarschmidt, Mayer-Bugström, and Sevon, *locc. cit.*) and the necessity for the use of chlorobenzene and a temperature of only 50° is shown by yields of 23% and 25% obtained with tetrachloroethane as solvent and with a temperature of 75° respectively.

Acenaphthene.—Acenaphthene (15·4 g., 1 mol.), tetrachloroethane (100 c.c.), hydrogen cyanide (16 c.c., 4 mols.), aluminium chloride (30 g., 2·25 mols.); time, 5 hours at 80°. Yield: 12·7 g., 70%. The procedure described above (phenanthrene) was then followed, and the light brown bisulphite compound obtained was boiled for 5 minutes with a slight excess of *N*-sulphuric acid. The oil obtained solidified on cooling and crystallisation from aqueous alcohol or light petroleum (b. p. 80—100°) yielded *acenaphthene-3-aldehyde* in colourless laminae, m. p. 87° (Found: C, 86·3; H, 5·7. $C_{13}H_{10}O$ requires C, 85·7; H, 5·5%). The aldehyde yielded a bright red solution with concentrated sulphuric acid and the following derivatives were obtained by the usual procedures: the *phenylhydrazone* crystallised from aqueous alcohol in orange needles, m. p. 140° (Found: N, 10·2. $C_{19}H_{16}N_2$ requires N, 10·3%), the 2 : 4-*dinitrophenylhydrazone* from alcohol in scarlet needles, m. p. 273° (Found: N, 15·1. $C_{19}H_{14}O_4N_4$ requires N, 14·7%), the *oxime* from light petroleum (b. p. 60—80°) in clusters of colourless needles, m. p. 126·5° (Found: N, 7·0. $C_{13}H_{11}ON$ requires N, 7·1%), the *semicarbazone* from methyl alcohol in small needles, m. p. 234° (Found: N, 17·3. $C_{14}H_{13}ON_3$ requires N, 17·6%), and the

aniline derivative from ether–light petroleum (b. p. 60—80°) in orange needles, m. p. 97° (Found: N, 5·4. $C_{19}H_{15}N$ requires N, 5·4%).

Oxidation of Acenaphthene-3-aldehyde.—The aldehyde (1 g.), oxidised with potassium permanganate (3·6 g.) according to the procedure described above for 1 : 6-dimethyl-4-naphthaldehyde, yielded a white powdery precipitate (0·7 g.). Washing with water and drying in a vacuum gave naphthalene-1 : 4 : 5-tricarboxylic acid (Found: equiv., 87·1. Calc., 86·7), which on heating yielded the anhydride, m. p. 243° (compare Graebe and Haas, *Annalen*, 1903, 327, 95).

Fluorene.—Fluorene (25 g., 1 mol.); chlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 4 mols.), aluminium chloride (60 g., 3 mols.); *time*, 5 *hours at* 70°. *Yield*: 22 g., 75·7%. The aldehyde was isolated through its bisulphite compound by the procedure adopted for diphenyl-4-aldehyde. Crystallisation from aqueous alcohol or light petroleum (b. p. 80—100°) yielded *fluorene-2-aldehyde* in colourless needles, m. p. 90° (Found: C, 86·3; H, 5·1. $C_{14}H_{10}O$ requires C, 86·6; H, 5·15%).

The influence of the solvent is very well illustrated with fluorene, since by replacement of the chlorobenzene by *o*-dichlorobenzene or tetrachloroethane, the above quantities and conditions being used, the yield is diminished to 62% and 52% respectively.

Fluorene-2-aldehyde readily yields the following derivatives: the *aniline* derivative crystallised from aqueous alcohol in pale yellow plates, m. p. 158° (Found: N, 5·2. $C_{20}H_{15}N$ requires N, 5·2%), the *phenylhydrazone* from alcohol in pale yellow leaflets, m. p. 202—203° (Found: N, 9·95. $C_{20}H_{16}N_2$ requires N, 10·0%), the *oxime* from light petroleum (b. p. 60—80°) in colourless plates, m. p. 156—157° (Found: N, 6·65. $C_{14}H_{11}ON$ requires N, 6·7%), and the *semicarbazone* from alcohol in colourless plates, m. p. 278° (Found: N, 16·6. $C_{15}H_{13}ON_3$ requires N, 16·7%).

Oxidation of Fluorene-2-aldehyde.—(a) *With alkaline potassium permanganate.* The aldehyde (1·9 g.) was oxidised with potassium permanganate as described above for dimethylnaphthaldehyde and yielded fluorenone-2-carboxylic acid (1·5 g.), which crystallised from alcohol in bright yellow needles, m. p. 338° with sublimation, unchanged by admixture with an authentic specimen, m. p. 338°, prepared as described below (Found: equiv., 223. Calc., 224) (Kruber, *Ber.*, 1932, 65, 1382, and Dziewonski and Schnayder, *Bull. intern. acad. polonaise*, 1930, *A*, 529, record m. p. 332° and sublimation at about 340° respectively).

(b) *With sodium dichromate.* The aldehyde (3 g.) in glacial acetic acid (100 c.c.) was heated at 100° for 3 hours with sodium dichromate (10 g.), and the mixture poured into water (300 c.c.). The resulting precipitate was washed with water and dried; crystallisation from alcohol yielded fluorenone-2-carboxylic acid (1·5 g.), m. p. and mixed m. p. 338°. The alcoholic liquor, on concentration and dilution with water, yielded fluorene-2-carboxylic acid (0·9 g.) in white prisms, m. p. 275° (decomp. and partial sublimation), unchanged by admixture with a specimen prepared as described below (Found: equiv., 209. Calc., 210). On oxidation with potassium permanganate the fluorene-2-carboxylic acid was converted into fluorenone-2-carboxylic acid.

Fluorene- and Fluorenone-2-carboxylic Acids.—2-Aminofluorene, prepared from fluorene by Diels's method (*Ber.*, 1901, 34, 1758), was converted into 2-cyanofluorene as described by Fortner (*Monatsh.*, 1904, 25, 447). Hydrolysis of 2-cyanofluorene (3·5 g.) with hydrochloric acid yielded fluorene-2-carboxylic acid (2 g.) in colourless prismatic needles, decomposing at 275° with partial sublimation (Fortner records m. p. > 265°). Oxidation of this acid (1·5 g.) yielded fluorenone-2-carboxylic acid (1·1 g.) in bright yellow needles, m. p. 338° with sublimation (Fortner records m. p. > 275°; Kruber; and Dziewonski and Schnayder, *locc. cit.*).

Fluorenone-2-carboxylic acid (1 g.), obtained by oxidation of fluorenealdehyde, was added to fused potassium hydroxide (10 g.). The cooled melt, treated according to the procedure described by Kruber (*loc. cit.*), yielded diphenyl-2 : 4′-dicarboxylic acid (0·9 g.) in colourless prisms, m. p. 271—272° (Found: equiv., 121·5. Calc., 121) (Kruber records m. p. 272°).

Conversion of Fluorene-2-aldehyde into 2-Methylfluorene.—To zinc (20 g.), amalgamated by standing with 5% aqueous mercuric chloride solution (40 c.c.) for 1 hour, fluorene-2-aldehyde (5 g.) and hydrochloric acid (1 part conc. acid : 2 parts of water by vol.) (40 c.c.) were added. The mixture was heated under reflux for about 8 hours with addition of small amounts of concentrated hydrochloric acid until the zinc had dissolved. Dilution with water (100 c.c.) and distillation in steam yielded 2-methylfluorene (1 g.), which crystallised from aqueous alcohol in colourless plates, m. p. 102—103° (Kruber, *loc. cit.*, records m. p. 104°).

Experiments with Chloromethyleneformamidine.—A mixture of chloromethyleneformamidine (Hinkel, Ayling, and Beynon, J., 1935, 676), powdered aluminium chloride, and the hydrocarbon in the requisite solvent was protected from moisture and heated, with frequent shaking,

in a water-bath. A series of experiments, in which the proportions of the reactants, the reaction temperature, and the period of heating were varied, was carried out with each hydrocarbon. Dark viscous liquids were obtained and the resulting aldehydes were isolated according to the procedure previously described for each aldehyde. The effect of varying the conditions was generally similar to that observed in the hydrogen cyanide synthesis with the same hydrocarbon. The following table gives the optimum conditions with the hydrocarbons studied; tetrachloroethane (50 c.c.) was used as solvent with the hydrocarbon (0·1 g.-mol.), the other proportions being referred to the hydrocarbon as unity. In no case here was the formation of a dialdehyde observed.

Hydrocarbon.	$(HCN)_2HCl$, mols.	$AlCl_3$, mols.	Reaction. Temp.	Hours.	% Yield of aldehyde.
Benzene	2·5	4·0	65°	5	75
Naphthalene	2·0	0·5	70	4	66
Anthracene	2·0	2·0	50	3	50
Hydrindene	2·0	0·5	50	4	60
Acenaphthene	1·0	2·0	50	1·5	90
Fluorene	1·25	1·25	50	4	70

Diphenyl-4-aldehyde and -4 : 4'-dialdehyde.—Diphenyl (15·4 g., 1 mol.), heated with chloromethyleneformamidine (20 g., 2·2 mols.) and aluminium chloride (40 g., 3 mols.) in chlorobenzene (50 c.c.) for 5 hours at 80°, yielded diphenyl-4-aldehyde, m. p. 60°. A similar resnlt was obtained with *o*-dichlorobenzene (50 c.c.) as the solvent. When tetrachloroethane (50 c.c.) was used as the solvent, the only aldehydic product was diphenyl-4 : 4'-dialdehyde, m. p. 145° (2·1 g.; 10%); phenylhydrazone, m. p. 278° (compare Ullmann, *Annalen*, 1904, **332**, 38). With less aluminium chloride (33·3 g., 2·5 mols.) and reaction at 60° for 6 hours in tetrachloroethane (50 c.c.), only dialdehyde (2·7 g.; 13%) was again obtained. In each tetrachloroethane experiment, the remainder of the diphenyl was partly unchanged and partly converted into a brown non-steam-volatile solid.

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University College, Swansea. [Received, January 7th, 1936.]

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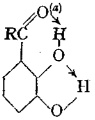
79. *Studies in Chelation. Part IV. Some Properties of 2 : 3-Dihydroxyphenyl Ketones.*

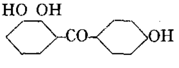
By Wilson Baker and A. R. Smith.

The properties of 2 : 3-dihydroxyphenyl ketones are of interest from the standpoint of chelation and because this type of grouping occurs in the dyes of the 2 : 3 : 4-trihydroxyphenyl ketone (Alizarin Yellow) class.

It was suggested in Part I (Baker, J., 1934, 1684) that the volatility and solubility of 2 : 3-dihydroxybenzaldehyde indicated a greater degree of chelation than the normal for a dihydroxybenzaldehyde, and, partly by analogy with 3-nitrocatechol, the structure (I; R = H) was proposed for the compound, in which the co-ordinate link (*a*) enhanced the usual feeble chelation between the two hydroxyl groups. The melting points of the dry and the wet substance are 106° and 84°, a difference of 22°.



(I.)



(II.)

(III.)

The same somewhat abnormal chelation for a catechol derivative appears to exist also in 2 : 3-dihydroxyacetophenone (I; R = CH_3), which has the same boiling point (245°) as catechol in spite of the increase in molecular weight. The low boiling point is significant

when it is recalled that the introduction of the CO·CH_3 group into the *o*-position of phenol *raises* the boiling point from 182° to 203°. Again, the difference between the melting points of wet and dry 2 : 3-dihydroxyacetophenone is much less than that for other dihydroxyacetophenones, as shown below, in spite of the fact that it has the lowest melting point.

	M. p. (dry).	M. p. (wet).	Difference.
2 : 3-Dihydroxyacetophenone	98°	71°	27°
2 : 4- ,,	142	78	64
2 : 5- ,,	202	160	42
2 : 6- ,,	157	108	49

Alone among the dihydroxyacetophenones the 2 : 3-compound has a powerful odour, resembling that of *o*-hydroxyacetophenone, and is easily soluble in organic solvents.

The relatively high degree of chelation of 2 : 3-dihydroxyacetophenone appears to be connected with the fact that it is a mordant dye. On cotton mordanted with alumina it gives a light yellow dyeing, which, however, is appreciably weaker than that given by 2 : 3 : 4-trihydroxyacetophenone (Alizarin Yellow C). This behaviour appears to be unique among the dihydroxyacetophenones; none of the isomerides mentioned above give noticeable dyeings on an alumina-mordanted material. [The highly chelated 2 : 4-diacetylresorcinol possesses marked mordant-dyeing properties, but the feebly chelated, isomeric 4 : 6-diacetylresorcinol is without this power (Baker, *loc. cit.*).] Similarly, 2 : 3-*dihydroxybenzophenone* (I; R = Ph) and 2 : 3 : 4'-*trihydroxybenzophenone* (II) give strong yellow dyeings with an alumina mordant, which are but little weaker than that given by 2 : 3 : 4-trihydroxybenzophenone (Alizarin Yellow A). These facts indicate that the hydroxyl group in position 4 in the dyes of the Alizarin Yellow series plays no essential part in the dyeing.

The 2 : 3-dihydroxyphenyl ketones were prepared from *o*-veratraldehyde by treatment with a Grignard reagent to give a secondary alcohol (III), oxidation of this with chromic acid to the corresponding ketone, and demethylation with hydrobromic acid. An alternative method was the interaction of a Grignard reagent with *o*-veratronitrile, which gave directly the 2 : 3-dimethoxyphenyl ketones.

Experimental.

2 : 3-Dimethoxyacetophenone was prepared by oxidising 2 : 3-dimethoxyphenylmethylcarbinol (Pauly and von Buttlar, *Annalen*, 1911, **383**, 284) with chromic acid (Klages, *Ber.*, 1903, **36**, 3589; Krannichfeldt, *ibid.*, 1913, **46**, 4017), and also by the following method. 2 : 3-Dimethoxybenzonitrile (10·2 g.) (Baker and Eastwood, J., 1929, 2907), dissolved in anhydrous ether (50 c.c.), was added to a solution of methylmagnesium iodide prepared from magnesium (1·5 g.), methyl iodide (9 g.), and ether (50 c.c.). After 12 hours, the mixture was refluxed for 1 hour and decomposed with dilute acetic acid, and the ethereal layer separated, washed with sodium carbonate solution, dried, and distilled, leaving a residue (6·5 g.) of almost pure 2 : 3-dimethoxyacetophenone.

2 : 3-Dimethoxyacetophenone (6·5 g.) was refluxed for 5 hours with hydrobromic acid (*d* 1·5) and acetic acid (50 c.c. of each) (compare Krannichfeldt, *loc. cit.*), the mixture then being poured into water and extracted with ether; from the extracts, after the treatment described above, 2 : 3-dihydroxyacetophenone was obtained, which separated from dilute methyl alcohol in pale yellow plates (4 g.), m. p. 97°.

2 : 3-*Dimethoxybenzhydrol*.—To a solution of phenylmagnesium bromide (prepared from magnesium 3·6 g., bromobenzene 15·7 g., and ether 150 c.c.) was added 2 : 3-dimethoxybenzaldehyde (24·9 g.) in ether (250 c.c.), and the whole heated on the steam-bath for 1 hour. The resulting magnesium compound was decomposed with ice and dilute acetic acid, and the ethereal layer treated as described above; the solid obtained, after contact with porous earthenware, crystallised from light petroleum in compact prisms, m. p. 79° (Found : C, 74·0; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%).

2 : 3-*Dimethoxybenzophenone*.—(A) To the preceding compound (20 g.) was added a solution of potassium dichromate (40 g.) in dilute sulphuric acid (170 c.c. of water and 35 c.c. of concentrated sulphuric acid) at 50°, and the whole vigorously stirred; the mixture boiled and slight cooling was necessary. After the initial reaction had abated, the mixture was stirred for 20

minutes, cooled, and extracted with ether. The extract was treated in the usual way, and 2 : 3-dimethoxybenzophenone obtained as a thick yellow oil, b. p. 210°/14 mm. (yield, 13·3 g.; 66%). The 2 : 4-*dinitrophenylhydrazone*, prepared from equal weights (0·5 g.) of the reactants dissolved in alcohol (6 c.c.) and concentrated sulphuric acid (1 c.c.), separated from alcohol as an orange crystalline powder, m. p. 152° (Found: N, 13·5. $C_{21}H_{18}O_6N_4$ requires N, 13·3%). (B) The Grignard reagent made from bromobenzene (2·6 c.c.), magnesium (0·6 g.), and ether (25 c.c.) was added to a solution of 2 : 3-dimethoxybenzonitrile (4·1 g.) in ether (25 c.c.). After 12 hours the product was decomposed with dilute acetic acid and shaken with a further quantity of ether, and the ethereal layer treated in the usual way.

2 : 3-*Dihydroxybenzophenone*.—2 : 3-Dimethoxybenzophenone (5 g.) was demethylated by the process described above [acetic acid, 50 c.c.; hydrobromic acid (*d* 1·5), 50 c.c.; 8 hours' refluxing]. From the washed and dried ethereal extract a solid was finally obtained, which, pressed on porous earthenware and crystallised from 20% alcohol, formed lustrous yellow plates, m. p. 65° (m. p. under water, 54°) (Found: C, 72·7; H, 4·7. $C_{13}H_{10}O_3$ requires C, 72·9; H, 4·7%). 2 : 3-*Dihydroxybenzophenone* dyes iron-mordanted cotton chocolate-brown, and with a chromium mordant a very weak greenish-yellow is prodnced. It forms a reddish solution in aqueous sodium hydroxide and gives a dark green ferric chloride reaction in alcoholic solution.

2 : 3 : 4'-*Trimethoxybenzhydrol*.—2 : 3-Dimethoxybenzaldehyde (16·6 g.) in ether (200 c.c.) was added to anisylmagnesium bromide prepared from *p*-bromoanisole (12·5 c.c.), ether (300 c.c.), and magnesium (5 g.), and the mixture warmed for 1 hour on the water-bath. After decomposition with dilute acetic acid, the ethereal layer was separated, shaken with sodium carbonate solution, dried, and distilled. The remaining oil was subjected to steam-distillation to remove *p*-bromoanisole, taken up in ether, and finally distilled under diminished pressure. The first fraction (b. p. 150°/15 mm.) was 2 : 3-dimethoxybenzaldehyde; the 2 : 3 : 4'-*trimethoxybenzhydrol* then distilled at 250°/17 mm. as a yellow viscous oil (Found: C, 70·0; H, 6·8. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·6%).

2 : 3 : 4'-*Trimethoxybenzophenone*.—(A) The preceding compound (12 g.) was added gradually to a vigorously stirred solution of potassium dichromate (24 g.) in water (100 c.c.) containing concentrated sulphuric acid (20 c.c.) at 50°. After being heated for 1 hour on the steam-bath, the mixture was cooled and extracted with ether. The dried extract yielded a residue, which solidified and then separated from dilute methyl alcohol in compact colourless crystals (9 g.), m. p. 86° (Found: C, 70·6; H, 6·2. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

2 : 3 : 4'-*Trihydroxybenzophenone* (II).—2 : 3 : 4'-Trimethoxybenzopbenone was demethylated with hydrobromic acid-acetic acid in the usual way, the mixture poured into water, and the solid collected and washed. Recrystallisation from dilute methyl alcohol (charcoal) gave minute, yellow, prismatic needles, m. p. 169° (Found: C, 63·0; H, 5·0. $C_{13}H_{10}O_4,H_2O$ requires C, 62·9; H, 4·9%). The substance gave an intense brownish-green colour with ferric chloride in alcoholic solution, and a deep olive-green in dilute alcohol. With iron and chromium mordants it gave a chocolate and a greenish-yellow dyeing respectively.

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THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, January 24th*, 1936.]

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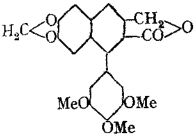
80. *The Constituents of Natural Phenolic Resins. Part IV. Synthesis of Dehydroanhydropicropodophyllin.*

By ROBERT D. HAWORTH and THOMAS RICHARDSON.

SPÄTH, WESELY, and KORNFELD (*Ber.*, 1932, **65**, 1536) prepared the optically inactive lactone, dehydroanhydropicropodophyllin, m. p. 266°, by converting podophyllotoxin into the isomeric picropodophyllin and dehydrogenating the latter with palladium-black, and on the basis of the Borsche–Späth formula for podophyllotoxin they represented this important degradation product as (I). The isomeric lactone (II), the synthesis of which was described in Part III of this series (J., 1935, 1576), differed from dehydroanhydropicropodophyllin, but Späth, Wesely, and Kornfeld's formula (I) was supported by the fact that the natural and the synthetic lactone were oxidised to the same dicarboxylic acid (III).

More direct proof of the accuracy of these views has now been obtained; a lactone having formula (I) has been synthesised, and its identity with dehydroanhydropicropodophyllin established.



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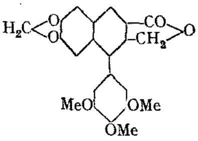

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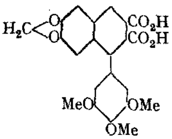
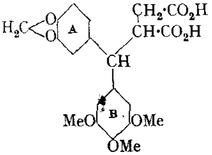


(III.)

The methods employed in Part II (J., 1935, 638) for the synthesis of the lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid were not applicable to the synthesis of (I). In the first place they require the preparation of (IV), and although compounds of this class are readily accessible when the rings A and B are identical, considerable difficulties are involved in the preparation of the unsymmetrical members of the class. Secondly, the subsequent conversion into the tetralonecarboxylic acid would lead to two isomeric products in a proportion determined by the relative nuclear activities of rings A and B. After several unsuccessful attempts had been made to overcome these difficulties, a new method was elaborated for the synthesis of compounds of type (I). It was found that safrole oxide and ethyl sodiomalonate reacted in alcoholic solution, yielding an oil which is considered to be *ethyl* β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone*-α-*carboxylate* (V; R = CO_2Et) and not the alternative carboxylate (VI; R = CO_2Et). The formula assigned to this lactone is, however, based entirely on analogy with the corresponding ethyl acetoacetate derivatives, which have been investigated more fully. The sodio-derivative of the lactone (V; R = CO_2Et) and 3 : 4 : 5-trimethoxybenzoyl chloride yielded *ethyl* α-(3 : 4 : 5-*trimethoxybenzoyl*)-β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone*-α-*carboxylate* (VII; R = CO_2Et), but the small yield and certain difficulties encountered in the hydrolysis of this lactone led to the abandonment of this route in favour of the corresponding ethyl acetoacetate compounds.



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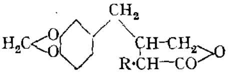

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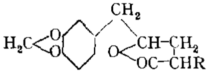
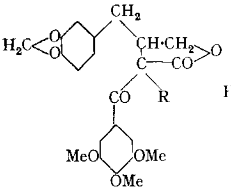


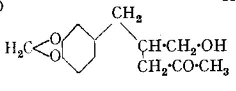
(VI.)

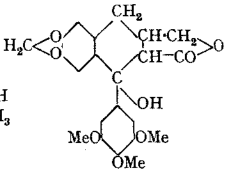
α-*Acetyl*-β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone* (V; R = $CO{\cdot}CH_3$) was prepared from safrole oxide and ethyl sodioacetoacetate, and this crystalline lactone underwent ketonic hydrolysis with hot dilute sodium hydroxide solution, yielding *methyl* γ-*hydroxy*-β-(3 : 4-*methylenedioxybenzyl*)*propyl ketone* (VIII). When the lactone (V; R = $CO{\cdot}CH_3$) was warmed with concentrated alcoholic potassium hydroxide, an oily lactone was obtained which gave the analytical figures required for the anticipated product of acid hydrolysis (V; R = H), and a similar oil was obtained by the action of strong alkalis on the corresponding ethyl malonate derivative (V; R = CO_2Et).

α-(3 : 4 : 5-*Trimethoxybenzoyl*)-α-*acetyl*-β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone* (VII; R = $CO{\cdot}CH_3$) was readily prepared from 3 : 4 : 5-trimethoxybenzoyl chloride and the sodio-derivative of the lactone (V; R = $CO{\cdot}CH_3$), and on hydrolysis with cold sodium hydroxide solution it yielded α-(3 : 4 : 5-*trimethoxybenzoyl*)-β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone* (VII; R = H). This crystalline lactone (VII; R = H), which could not be prepared

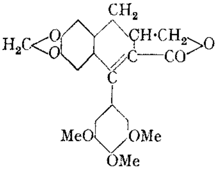
directly from safrole oxide and ethyl sodio-3 : 4 : 5-trimethoxybenzoylacetate, was isomerised by the action of methyl-alcoholic hydrogen chloride into the *lactone* of 1-*hydroxy*-

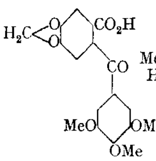

(VII.)

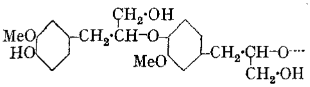

(VIII.)


(IX.)

6 : 7-*methylenedioxy*-1-(3′ : 4′ : 5′-*trimethoxyphenyl*)-3-*hydroxymethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylic acid* (IX). Dehydration of (IX) with potassium hydrogen sulphate at 180° gave the *lactone* of 6 : 7-*methylenedioxy*-1-(3′ : 4′ : 5′-*trimethoxyphenyl*)-3-*hydroxymethyl*-3 : 4-*dihydronaphthalene*-2-*carboxylic acid* (X), which was converted into 3′ : 4′ : 5′-trimethoxy-4 : 5-methylenedioxybenzophenone-2-carboxylic acid (XI). This acid was identical with the acid which Späth, Wesely, and Nadler (*Ber.*, **1933**, **66**, 128) obtained by oxidation of picropodophyllin and, if the remote possibility of seven-membered ring formation is excluded, the isolation of acid (XI) provides conclusive evidence for the structures (V), (VII), (IX), and (X).


(X.)


(XI.)


(XII.)

The lactone (X) was converted into the lactone of 6 : 7-methylenedioxy-1-(3′ : 4′ : 5′-trimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid (I), m. p. 267°, either by heating with palladium-black or by the action of lead tetra-acetate in acetic acid solution. The synthetical lactone (I) was identical in all respects with dehydroanhydropicropodophyllin prepared from podophyllotoxin as described by Späth, Wesely, and Kornfeld (*loc. cit.*).

The reactions described are being exploited in other directions and the polymerisation of compounds of the safrole oxide type is also being investigated. The known reaction between ethylene oxides and phenoxides (Boyd and collaborators, J., 1908, **93**, 838; 1909, **95**, 1807; 1910, **97**, 1788; 1914, **105**, 2117) may find a particularly interesting application in the case of eugenol oxide, which under suitable conditions may polymerise to products structurally related to Freudenberg's lignin formula (XII) (*Ber.*, 1929, **62**, 1822; *Annalen*, **1935**, **518**, 78).

Experimental.

Ethyl β-(3 : 4-*Methylenedioxybenzyl*)*butyrolactone*-α-*carboxylate* (V; R = CO_2Et).—Safrole oxide (4 g.) (Fourneau and Tiffeneau, *Compt. rend.*, 1905, **140**, 1595; **141**, 662) was added to ethyl sodiomalonate (prepared from sodium, 0·6 g., and ethyl malonate, 5 g.) in ethyl alcohol (30 c.c.). The sodio-derivative of (V; R = CO_2Et), which slowly separated, was collected after 48 hours and decomposed with water or dilute sulphuric acid, and the resulting oil extracted with ether and dried. The *lactone* (V; R = CO_2Et) (1·5 g.) was obtained as a colourless oil, b. p.

210—215°/0·5 mm., readily soluble in the usual organic solvents (Found: C, 61·7; H, 5·7. $C_{13}H_{16}O_6$ requires C, 61·6; H, 5·5%).

Ethyl α-(3 : 4 : 5-*Trimethoxybenzoyl*)-β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone*-α-*carboxylate* (VII; R = CO_2Et).—The lactone (V; R = CO_2Et) (2 g.) was allowed to react with "molecular" sodium (0·15 g.) in benzene (20 c.c.) for 12 hours. 3 : 4 : 5-Trimethoxybenzoyl chloride (2 g.) was added, and the mixture heated on the water-bath for 18 hours. After the addition of water, the benzene layer was dried, the solvent removed, and the residual oil crystallised by addition of a little methyl alcohol. The *lactone* (VII; R = CO_2Et) separated from methyl alcohol, containing a small amount of chloroform, in colourless needles, m. p. 156—157° (Found: C, 59·5; H, 5·4. $C_{25}H_{26}O_{10},H_2O$ requires C, 59·5; H, 5·6%). The yield was small.

α-*Acetyl*-β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone* (V; R = $CO{\cdot}CH_3$).—Safrole oxide (24 g.) was added to a solution of ethyl sodioacetoacetate (prepared from sodium, 3 g., and ethyl acetoacetate, 18 g.) in ethyl alcohol (100 c.c.). After 3 days, water was added, neutral impurities removed with ether, the alkaline liquors acidified and extracted with benzene, and the solvent and unchanged ethyl acetoacetate removed under reduced pressure. The residue crystallised from ether–light petroleum (b. p. 40—60°) in colourless needles (11 g.), m. p. 91—92° (Found: C, 63·7; H, 5·2. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·2%). This *lactone* (V; R = $CO{\cdot}CH_3$) is soluble in dilute sodium hydroxide solution and it gives a violet ferric test.

Methyl γ-*Hydroxy*-β-(3 : 4-*methylenedioxybenzyl*)*propyl Ketone* (VIII).—The lactone (V; R = $CO{\cdot}CH_3$) (0·6 g.) was boiled with 2% sodium hydroxide solution (20 c.c.) for 6 hours. The oil which gradnally separated, and solidified on cooling, was collected; it crystallised from light petroleum (b. p. 60—80°) in slender needles, m. p. 79—80°, which gave no coloration with ferric chloride (Found: C, 65·8; H, 6·8. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%).

β-(3 : 4-*Methylenedioxybenzyl*)*butyrolactone* (V; R = H) was prepared by hydrolysing the lactone (V; R = $CO{\cdot}CH_3$) with 20% methyl-alcoholic potassium hydroxide (10 parts) for 6 hours on the water-bath. After dilution with water, most of the methyl alcohol was removed by distillation and neutral impurities were removed in ether. The alkaline layer was acidified and boiled for 5 minutes, and the oil isolated with ether; it distilled at 183—186°/0·5 mm. (Found: C, 65·3; H, 5·7. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%). A similar oil (Found: C, 65·2; H, 5·6%) was obtained by hydrolysing (V; R = CO_2Et) with 10% methyl-alcoholic potassium hydroxide and heating the acidic product at 180° for 1 hour.

α-(3 : 4 : 5-*Trimethoxybenzoyl*)-β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone* (VII; R = H).—The lactone (V; R = $CO{\cdot}CH_3$) (11 g.) was added to "molecular" sodium (1 g.) in benzene (100 c.c.). After 12 hours, 3 : 4 : 5-trimethoxybenzoyl chloride (10 g.) was added; the mixture was kept for 12 hours at room temperature and then boiled for 1 hour. Water was added, the benzene layer washed with very dilute sodium hydroxide solution and dried, and the solvent removed. The product (VII; R = $CO{\cdot}CH_3$), which did not crystallise, was taken up in ether (100 c.c.) and shaken with 5% sodium hydroxide solution (50 c.c.) for 12 hours. The alkaline solution was acidified and extracted with chloroform, and the extract shaken with sodium bicarbonate solution in order to remove traces of 3 : 4 : 5-trimethoxybenzoic acid. The chloroform was removed, and the residue crystallised from methyl alcohol; colourless needles (7 g.), m. p. 110—111°, were obtained (Found: C, 63·8; H, 5·2. $C_{22}H_{22}O_8$ requires C, 63·8; H, 5·4%). This *lactone* (VII; R = H) gave a reddish-purple ferric test.

Lactone of 1-*Hydroxy*-6 : 7-*methylenedioxy*-1-(3′ : 4′ : 5′-*trimethoxyphenyl*)-3-*hydroxymethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylic Acid* (IX).—The lactone (VII; R = H) (2 g.) was boiled with methyl-alcoholic hydrogen chloride (20 c.c.) for ½ hour. The product, isolated with chloroform, crystallised from methyl alcohol in slender needles (1·4 g.), m. p. 138—139° (Found: C, 63·8; H, 5·6. $C_{22}H_{22}O_8$ requires C, 63·8; H, 5·4%). This *lactone* (IX) gave no coloration with ferric chloride, bnt it dissolved in concentrated sulphuric acid to a green solution which became red on standing and purple on warming.

Lactone of 6 : 7-*Methylenedioxy*-1-(3′ : 4′ : 5′-*trimethoxyphenyl*)-3-*hydroxymethyl*-3 : 4-*dihydronaphthalene*-2-*carboxylic Acid* (X).—The lactone (IX) (1 g.) was heated with potassium hydrogen sulphate (2 g.) for ¾ hours at 180°. The product, isolated with chloroform, crystallised from methyl alcohol in slender needles (0·8 g.), m. p. 248—249° (Found: C, 66·7; H, 5·0. $C_{22}H_{20}O_7$ requires C, 66·6; H, 5·0%). This *lactone* (X) gave a colour reaction with concentrated sulphuric acid similar to that described above for the lactone (IX). The lactone (X) (1 g.) was boiled with 2% methyl-alcoholic potassium hydroxide (20 c.c.) for 10 minutes. Water was added, the alcohol completely removed by distillation, and 3% aqueous potassium permanganate (200 c.c.) gradually added to the cold solution. After the manganese dioxide had been removed, the filtrate was acidified and the precipitate collected. 3′ : 4′ : 5′-Trimethoxy-4 : 5-methylenedioxy-

benzophenone-2-carboxylic acid (XI) separated from dilute acetic acid in small crystals (0·2 g.), m. p. 215—216° (Found: C, 59·6; H, 4·5. Calc. for $C_{18}H_{16}O_8$: C, 60·0; H, 4·5%). The methyl ester and 3' : 4' : 5'-trimethoxy-3 : 4-methylenedioxybenzophenone melted at 127—128° and 126—127° respectively. Späth, Wesely, and Nadler (*loc. cit.*) give 214—216°, 128—129°, and 125—127° for the acid, the methyl ester, and the benzophenone derivative respectively.

Lactone of 6 : 7-*Methylenedioxy*-1-(3' : 4' : 5'-*trimethoxyphenol*)-3-*hydroxymethylnaphthalene*-2-*carboxylic Acid* (*Dehydroanhydropicropodophyllin*) (I).—(*a*) The lactone (X) (0·6 g.) was dissolved in acetic acid (10 c.c.) at 75°, and lead tetra-acetate (1·2 g.) added; after 15 minutes, water was added, and the product isolated with chloroform. (*b*) The lactone (X) (0·1 g.) and palladium-black (0·02 g.) were heated at 240°/0·1 mm., for 6 hours, and the sublimate collected. The product from either (*a*) or (*b*) crystallised from methyl alcohol or glacial acetic acid in colourless needles, m. p. 267—268° (Found: C, 66·9; H, 4·7. Calc. for $C_{22}H_{18}O_7$: C, 67·0; H, 4·6%), and no depression in m. p. was observed when the synthetic specimen was mixed with dehydroanhydropicropodophyllin, m. p. 265—266°, prepared from podophyllotoxin. The synthetic and the natural lactone were identical in crystalline form and had similar solubilities in organic solvents. On treatment with cold concentrated sulphuric acid, both specimens dissolved to very pale yellow solutions, which became purple on warming. The addition of a crystal of sodium nitrate to the cold sulphuric acid solutions produced a blood-red colour. The synthetic lactone was converted into the dibasic acid (III) by the action of either sodium hypobromite or potassium permanganate and the oxdation product was identified by the preparation of the anhydride, m. p. 300°, and the dimethyl ester, m. p. 207° (see J., 1935, 1581).

Our thanks are due to the Durham County Council Education Department for a scholarship awarded to one of us (T. R.).

University of Durham, Armstrong College,
Newcastle-upon-Tyne. [*Received, January 20th*, 1936.]

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81. *Preparation of Aldehydes from Nitriles (Stephen's Method). γ-Phthalimidobutaldehyde.*

By F. E. King, Philibert L'Ecuyer, and (in part) Harry T. Openshaw.

The marked tendency of certain aliphatic aldehydes, such as those used in alkaloid synthesis, to undergo irreversible self-condensation often renders them difficult of access except from nitriles, which, being converted into the so-called iminochlorides, can be reduced by means of anhydrous stannous chloride at the ordinary temperature (Stephen, J., 1925, 127, 1874). The products are double salts of the type $(R\cdot CH{:}NH,HCl)_2,SnCl_4$, from which the aldehydes may be obtained merely by the action of water.

Of the many illustrations offered by Stephen, α-naphthonitrile and *o*-toluonitrile alone give poor yields, but in three recently investigated examples, *viz.*, γ-phenoxy-α-methylbutaldehyde (King and Robinson, J., 1933, 273), γ-phthalimido-α-methylbutaldehyde (King, Liguori, and Robinson, *ibid.*, p. 1477), and γ-phenoxybutaldehyde (forthcoming publication), no precipitation of stannichloride occurred unless the reactants were heated for some time; the good yields normally associated with the method were then obtained. Even under these more drastic conditions, however, the two exceptional nitriles mentioned by Stephen (*loc. cit.*) gave no noticeable improvement in yield.

Prior to the 1925 memoir of Stephen, several aromatic aldehydes were synthesised by Sonn and Müller from anilides, these first reacting with phosphorus pentachloride to give iminochlorides, $R\cdot CCl{:}NPh$, which were reduced by stannous chloride under conditions parallel with those used in the Stephen method (*Ber.*, 1919, 52, 1927; Houben-Weyl, "Die Methoden der Organischen Chemie," 1923, III, 398). In view of the failure of *o*-toluonitrile to afford more than a small proportion of the related aldehyde, it is of interest to record that, by applying the process of Sonn and Müller to *o*-toluanilide, almost quantitative yields have now been obtained.

The method of Stephen has been extended to the preparation of *γ-phthalimidobutaldehyde*, which is of possible synthetical value. The requisite nitrile (Gabriel, *Ber.*, 1889, 22,

3337) was obtained by improved methods from γ-phthalimidobutyric acid through the usual intermediates.

EXPERIMENTAL.

α-Naphthaldehyde.—Hydrogen chloride was passed into a suspension of anhydrous stannous chloride in dry ether (9 g. in 35—40 c.c., *i.e.*, approximately the proportion recommended by Stephen). Saturation was expedited by cooling to 0°; the solid was then completely dissolved without the formation of a second layer. α-Naphthonitrile (5 g.) was then added. After 12 hours, the homogeneous liquid deposited a small amount of stannichloride, which refluxing for 6 hours and re-saturation with hydrogen chloride at 0° only slightly augmented. The precipitate was collected and decomposed with warm water, and the aldehyde (less than 1 g.) extracted with ether. The 2 : 4-*dinitrophenylhydrazone* crystallised from a fairly large volume of acetic acid in a deep yellow mass of minute needles (Found: C, 60·6; H, 3·5. $C_{17}H_{12}O_4N_4$ requires C, 60·7; H, 3·6%).

o-*Tolualdehyde.*—Although three experiments were made under various conditions, only a very small yield of aldehyde was obtainable from *o*-toluonitrile. To effect its preparation by the method of Sonn and Müller (*loc. cit.*), *o*-toluic acid (25 g.) was converted by boiling thionyl chloride (40 c.c.) into the acid chloride, which on dilution with benzene (60 c.c.) and addition to an ice-cold chloroform solution (200 c.c.) of aniline (35 g.) afforded *o*-toluanilide. By evaporating the washed and dried solution, and crystallising the residue from benzene, it was obtained as colourless needles, m. p. 125—126°. The gentle reaction between phosphorus pentachloride (10 g.) and the anilide (10 g.), dissolved in toluene (35 c.c.), began at 50° and was completed at 100°; both solvent and phosphorus oxychloride were then removed under diminished pressure. On addition of the residual pale red syrup to a solution prepared from ether (100 c.c.) and stannous chloride (25 g.) saturated at 0° with hydrogen chloride, a yellow precipitate began to separate. After several hours the solid was collected and placed in boiling dilute hydrochloric acid. The aldehyde (4·9 g.) collected in the steam distillate and was removed by ether extraction. It was recognised by the semicarbazone, m. p. 210—211°, and by the 2 : 4-*dinitrophenylhydrazone*, which crystallised from acetic acid in orange-red rectangular plates, m. p. 193—194° (30° depression when mixed with the hydrazine) (Found, after drying at 120°: C, 56·2; H, 3·9. $C_{14}H_{12}O_4N_4$ requires C, 56·0; H, 4·0%).

Ethyl β-Phthalimidoethylmalonate and γ-Phthalimidobutyric Acid.—Robinson and Suginome (J., 1932, 307) have shown that the use of alcohol as a solvent for condensations which involve phthalo-β-bromoethylimide and sodio-compounds may lead to inferior yields owing to a by-reaction, so in a repetition of Aschan's preparation of ethyl β-phthalimidoethylmalonate (*Ber.*, 1891, **24**, 2449), the powdered bromide (70 g.), with 2 g. of sodium iodide, was added to a benzene suspension of ethyl sodiomalonate prepared by refluxing ethyl malonate (70 g.) and pulverised sodium (9·4 g.) in dry benzene (200 c.c.) for 2 hours on a steam-bath. After 16 hours' heating under reflux, the mass was made neutral with acetic acid and exhaustively steam-distilled. The non-volatile residue was removed by ether and fractionated, the substituted malonate (58 g.) having b. p. 225—235°/4·5 mm.

To hydrolyse the ester without removing the phthalimido-group, Radde (*Ber.*, 1922, **55**, 3177) used cold hydrobromic acid (yield, 60%), but the following method, based on the preparation of γ-phthalimido-α-methylbutyric acid (King, Liguori, and Robinson, *loc. cit.*), is more satisfactory. A mixture of acetic anhydride (80 c.c.) and concentrated hydrochloric acid (120 g.) with the ester (10 g.) in solution was boiled in an open flask for exactly 50 mintues; the remaining solvents were then removed under diminished pressure at 100°. The residue (7·5 g.), after one crystallisation from alcohol, had m. p. 167—168° and was almost pure, the m. p. of β-phthalimidoethylmalonic acid being given by Radde as 168°. It was decarboxylated by heating for 5—10 minutes in an oil-bath at 180°; the residue, crystallised from benzene and then from aqueous alcohol (50%), gave γ-phthalimidobutyric acid in colourless prisms, m. p. 116—117° (Found: C, 61·8; H, 4·9. Calc. for $C_{12}H_{11}O_4N$: C, 61·8; H, 4·7%). Gabriel and Colman (*Ber.*, 1908, **41**, 513) record m. p. 117—118° after sintering at *ca.* 115°.

γ-Phthalimidobutyramide.—γ-Phthalimidobutyric acid (10 g.) was refluxed with thionyl chloride (20 c.c.) for ½ hour, and the solution evaporated to dryness under reduced pressure at 100°. The residual yellow crystalline acid chloride was dissolved in absolute ether (150 c.c.), and the solution saturated at 0—10° with dry ammonia. The resulting white paste was freed from solvent by filtration, and shaken with water to dissolve ammonium chloride. Gabriel and Colman (*loc. cit.*) record for γ-phthalimidobutyramide m. p. 165—166°, and our product (9·5 g.), after one

crystallisation from alcohol, had m. p. 166—167°, which further treatment did not advance beyond 167° (Found : C, 62·1 ; H, 5·3. Calc. for $C_{12}H_{12}O_3N_2$: C, 62·1 ; H, 5·2%).

γ-Phthalimidobutyronitrile (cf. Gabriel, *loc. cit.*).—The amide (10 g.) and thionyl chloride (20 g.) were refluxed for ½ hour, and the excess of dehydrating agent then removed under diminished pressure. The residue, which immediately solidified, was wasbed with sodium bicarbonate solution and then with water. The dried product (9·2 g.), crystallised from benzene–light petroleum, yielded phthalimidobutyronitrile, m. p. *ca.* 81°, and one recrystallisation from alcohol gave the pure substance, m. p. 81—82° (Found : C, 67·4; H, 4·8. Calc. for $C_{12}H_{10}O_2N_2$: C, 67·3; H, 4·7%).

γ-Phthalimidobutaldehyde.—Unlike the three recent examples cited in the introduction, when the nitrile (6 g.) was added to stannous chloride (9 g.) in absolute ether (50 c.c.) saturated with hydrogen chloride, the stannichloride was slowly precipitated at room temperature. After 12 hours, the solid was collected, but it proved unusually stable towards water, and as the resultant *aldehyde* rapidly polymerised, the tin salt was best hydrolysed by being mechanically shaken with equal volumes of ether and water for 3 hours. After filtration, the ethereal solution was rapidly dried (magnesium sulphate) and evaporated at room temperature. The residue (4·5 g.) was a colourless oil, but it shortly became turbid owing to the production of an amorphous polymeride. The 2 : 4-*dinitrophenylhydrazone*, prepared at room temperature, crystallised from acetic acid in yellow minute prisms, m. p. 184° (Found : N, 17·3. $C_{18}H_{15}O_6N_5$ requires N, 17·6%).

One of the authors (P. L'E.) thanks the Rhodes Trustees for the award of a scholarship.

The Dyson Perrins Laboratory, Oxford University. [*Received, January 27th*, 1936.]

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82. *Digitalis Glucosides. Part VI. The Existence of Two Anhydrodigoxigenins.*

By Sydney Smith.

In Part IV (J., 1935, 1050) it was shown that digitoxigenin, when treated with dilute acids, loses its single tertiary hydroxyl group and forms a mixture of the $\Delta^{14:15}$- and $\Delta^{14:8}$-unsaturated anhydrogenins, which can be separated by fractional crystallisation into the two isomerides. Since the constitution of digoxigenin (Part V; J., 1935, 1305) is similar to that of digitoxigenin, the former also should give rise to two anhydrogenins. This is in fact the case. The action of dilute acids on digoxigenin (Part II; J., 1930, 2479) gives a non-homogeneous product, from which the crystalline anhydrogenin, m. p. 182°, can be isolated as originally described. The mother-liquors from the crystallisation of this anhydrogenin do not lend themselves to crystallisation and a second isomeride was not isolated from this source. Eventually it was found that, when digoxigenin is dissolved in concentrated hydrochloric acid, an unstable *chloro*-compound is formed, which is rapidly decomposed by water to give the expected second ***monoanhydrodigoxigenin***, m. p. 192°. As in the case of anhydrodigitoxigenin, the isomeride of higher m. p. is termed the α-compound and the previously described anhydrodigoxigenin, m. p. 182°, must now be distinguished as the β-compound. Both isomerides give the Legal reaction and therefore retain the double bond in the lactone group at $\Delta^{20:21}$ without displacement and retain the two secondary hydroxyl groups, since each forms a diacetate and on oxidation gives rise to the expected diketone.

Additional evidence for the similarity in constitution of digitoxigenin and digoxigenin is afforded by a comparison of the specific rotations of the four anhydrogenins as follows : $[\alpha]_{5461}^{20°} = +43·7°$ and $+46·0°$ for α-anhydrodigitoxigenin and α-anhydrodigoxigenin respectively and $-17·3°$ and $-16·3°$ for the corresponding β-compounds (in methyl alcohol in each case).

Note.—Owing to a typographical error the sign of the rotation of β-anhydrodigoxigenin is shown as + in Part II (J., 1930, 2479).

Experimental.

α-Anhydrodigoxigenin.—Digoxigenin (5 g.) was dissolved in concentrated hydrochloric acid (37 c.c.) at 10°. On keeping over-night in a refrigerator and stirring, 3·3 g. of an unstable *chloro*-

compound crystallised. It frothed at 120° and then melted at 185°. It was rapidly decomposed by water. A portion of the crystals after exposure to the air for a short time was stirred with water, the resulting anhydrogenin removed by filtration, and the liberated hydrochloric acid was determined by titration (Fonnd : Cl, 9·5. $C_{23}H_{33}O_4Cl$ requires Cl, 8·7%).

The chloro-compound was conveniently converted into *α-anhydrodigoxigenin* by crystallisation from hot aqueous methyl alcohol. This formed needles, m. p. 192°, $[\alpha]_{5461}^{20°}$ + 46° (in methyl alcohol, c = 1), readily soluble in acetone and methyl alcohol and moderately easily soluble in benzene, chloroform, ether, and ethyl acetate. It gave a red colour in the Legal test for $\Delta^{\beta\gamma}$-unsaturated lactones [Found (air dry): C, 67·6; H, 8·9; loss on drying, 9·3. $C_{23}H_{32}O_4,2H_2O$ requires C, 67·6; H, 8·9; H_2O, 8·8%. Found (dried at 100°): C, 74·1; H, 8·7. $C_{23}H_{32}O_4$ requires C, 74·2; H, 8·7%. Lactone titration: 13·78 mg. required 0·36 c.c. 0·1N-potassium hydroxide. One equiv. requires 0·37 c.c.].

The *diacetate*, prepared by the action of acetic anhydride in pyridine solution at laboratory temperature, crystallised from aqueous methyl alcohol in needles, m. p. 155°, $[\alpha]_{5461}^{20°}$ + 68·0° (in methyl alcohol, c = 0·7) (Found: C, 71·2; H, 8·1; Ac, 21·7. $C_{27}H_{36}O_6$ requires C, 71·0; H, 8·0; Ac, 18·8%).

α-Anhydrodigoxigenone.—α-Anhydrodigoxigenin (1 g.) was dissolved in a mixture of glacial acetic acid (20 c.c.) and water (5 c.c.) with the aid of heat. The solution was cooled to 20° and treated immediately with Kiliani's chromic acid solution (5 c.c.), being cooled at the same time so that the temperature did not rise. After dilution with water and keeping in the refrigerator for 20 hours, a crystalline solid (0·55 g.) separated, m. p. 165°. After crystallisation from dilute methyl alcohol the *ketone* melted at 178° and had the specific rotation $[\alpha]_{5461}^{20°}$ + 136° (in methyl alcohol, c = 0·8). It was sparingly soluble in ethyl acetate, benzene, and methyl alcohol, more soluble in acetone, but crystallised readily from hot aqueous acetone, or aqueous methyl alcohol. It gave a red colour in the Legal test (Found: C, 74·7; H, 7·6. $C_{23}H_{28}O_4$ requires C, 75·0; H, 7·7%).

The oxidation mother-liquor after removal of this substance was extracted with chloroform. The extract, after being washed with sodium carbonate solution and dried with magnesium sulphate, gave on evaporation a residue (0·4 g.), which crystallised from aqueous methyl alcohol in needles, m. p. 187°. The m. p. was raised by repeated crystallisation from aqueous methyl alcohol and from ethyl acetate to 215°. The substance was still apparently not quite pure and requires further investigation. It gives the Legal reaction for $\Delta^{\beta\gamma}$-lactones.

The *semicarbazone* was prepared from the ketone (0·1 g.) in methyl-alcoholic solution, semicarbazide hydrochloride (0·1 g.) in a little water, and potassium acetate (0·15 g.) in methyl alcohol at laboratory temperature. After recrystallisation from alcohol, in which it was sparingly soluble, it formed micro-needles, m. p. 235° (decomp.) (Found: N, 9·8. $C_{24}H_{31}O_4N_3$ requires N, 9·9%).

The *dioxime*, prepared by boiling the ketone in methyl-alcoholic solution with a reagent prepared from hydroxylamine hydrochloride and potassium acetate, could not be crystallised (Found: N, 6·9. $C_{23}H_{30}O_4N_2$ requires N, 7·0%).

The microanalyses were carried out by Mr. A. Bennett and Mr. H. C. Clarke, to whom I wish to express my thanks.

WELLCOME CHEMICAL WORKS, DARTFORD. [*Received, February 4th,* 1936.]

83. *The Action of Ammonia upon Esters.*

By F. D. CHATTAWAY.

THE behaviour of esters under the action of ammonia affords a striking example of the influence of substituted atoms or groups upon the reactivity of the carbon atoms of an aliphatic chain.

When ammonia, an amine, or a hydrazine reacts with an ester, an amide or a hydrazide is usually formed together with the alcohol corresponding to the original ester. This type of reaction is so common that it has come to be regarded as the invariable way in which such reactions occur. It appears to be initiated by the greater attraction which

the donor molecule, ammonia, has for the kationoid carbon of the acyl group than for the electron-repelling alkyl group :

$$\mathrm{R{-}\overset{+\delta}{\underset{\|}{C}}{\cdot}OR'} \xrightarrow{NH_3} \mathrm{R{-}\underset{\|}{C}{\cdot}NH_2 + HOR'}$$
$$\mathrm{O} \qquad\qquad\qquad \mathrm{O}$$

If this electronic state could be reversed by the introduction of a powerful kationoid centre in the alkyl group itself, then the donor molecule might attack not only the acyl group but to a greater or less extent the alkyl group, so that amines and hydrazines together with a salt of the ester acid would result :

$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{\cdot}O{\cdot}\overset{+\delta}{C}\!:} \xrightarrow{NH_3} \mathrm{R{\cdot}\underset{\underset{O}{\|}}{C}{\cdot}OH + H_2N{\cdot}C\!:}$$

Such a condition is realised in the acetic esters of the $\gamma\gamma\gamma$- and $\gamma\gamma\delta$-trichloro-α-nitro-β-hydroxy-paraffins (Chattaway and Witherington, J., 1935, 1178),

$$\mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}\overset{+\delta}{C}H{<}^{CCl_3}_{CH_2{\cdot}NO_2}} \quad \text{and} \quad \mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}\overset{+\delta}{C}H{<}^{CCl_2{\cdot}CHCl{\cdot}CH_3}_{CH_2{\cdot}NO_2}},$$

where in the highly substituted propyl and amyl groups both the CCl_3 and the $CCl_2{\cdot}CHCl{\cdot}CH_3$, and still more the $CH_2{\cdot}NO_2$ group are strongly electron-attracting. As a result, the carbon atom attached to these electron-attracting groups has become so kationoid that when the esters are acted upon by a donor molecule, such as ammonia, a primary amine, or a hydrazine, the carbon attached to the two kationoid groups and not the carbon atom of the carbonyl group becomes the point of attack and the resulting fission of the ester therefore yields a salt of acetic acid and an amine, an aniline, or a hydrazine. For example, when $\gamma\gamma\gamma$-trichloro-α-nitro-β-acetoxypropane reacts with ammonia, *$\gamma\gamma\gamma$-trichloro-α-nitro-β-aminopropane* and ammonium acetate are formed :

$$\mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}CH{<}^{CCl_3}_{CH_2{\cdot}NO_2}} \xrightarrow{NH_3} \mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}NH_4 + H_2N{\cdot}CH{<}^{CCl_3}_{CH_2{\cdot}NO_2}}$$

and similarly $\gamma\gamma\delta$-trichloro-α-nitro-β-acetoxypentane yields ammonium acetate and *$\gamma\gamma\delta$-trichloro-α-nitro-β-aminopentane*, $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NO_2$.

Precisely similar reactions occur when *p*-toluidine reacts with these esters, $CCl_3{\cdot}CH(NH{\cdot}C_6H_4Me){\cdot}CH_2{\cdot}NO_2$ and $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(NH{\cdot}C_6H_4Me){\cdot}CH_2{\cdot}NO_2$, being formed, and when they react with phenylhydrazine the corresponding *hydrazines* $CCl_3{\cdot}CH(NH{\cdot}NHPh){\cdot}CH_2{\cdot}NO_2$ and $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(NH{\cdot}NHPh){\cdot}CH_2{\cdot}NO_2$ result.

The substituted amines and hydrazines thus formed show the usual behaviour of such compounds, forming, for example, stable well-characterised salts and acyl derivatives, the two *acetamido*-compounds crystallising especially well.

EXPERIMENTAL.

$\gamma\gamma\gamma$-Trichloro-α-nitro-β-aminopropane.—A solution of 25 g. of $\gamma\gamma\gamma$-trichloro-α-nitro-β-acetoxypropane (Chattaway and Witherington, J., 1935, 1179) in 30 c.c. of absolute alcohol (99·5%) was cooled in ice, saturated with dry ammonia, and kept at the ordinary temperature, protected from moisture, for 2 days. Most of the alcohol and any excess of ammonia were then evaporated on a water-bath, best under somewhat diminished pressure. A slight smell of acetamide was noticed during the evaporation. Excess of dilute hydrochloric acid was then added and the liquid was warmed with animal charcoal, filtered, and evaporated to dryness. The dry mixture of the hydrochlorides of ammonia and $\gamma\gamma\gamma$-trichloro-α-nitro-β-aminopropane obtained was washed with a small quantity of an alcoholic solution of hydrogen chloride and dissolved in a little water. The solution was strongly cooled in a freezing mixture, and the *$\gamma\gamma\gamma$-trichloro-α-nitro-β-aminopropane* liberated by cautious addition of a concentrated solution of potassium hydroxide. As the base dissolves readily in a strongly alkaline solution, any excess of alkali must be avoided. It separated as a liquid, which was best extracted by ether and obtained by distillation in a vacuum as a pale yellow liquid, b. p. 108°/2 mm. (Found : Cl, 57·1. $C_3H_5O_2N_2Cl_3$ requires Cl, 57·3%). The *hydrochloride* crystallised from dilute hydrochloric

acid in nodular aggregates of small, almost colourless prisms with a faint yellow tint (Found: Cl as HCl, 14·7; total Cl, 58·4. $C_3H_5O_2N_2Cl_3$,HCl requires Cl as HCl, 14·6; total Cl, 58·2%).

When the base was warmed with a slight excess of acetic anhydride, it yielded *γγγ-trichloro-α-nitro-β-acetamidopropane*, CCl_3·CH(NHAc)·CH_2·NO_2, which crystallised from hot alcohol, in which it was readily soluble, in clusters of long transparent prisms, almost colourless with a very faint yellow tint, m. p. 137° (Found: Cl, 42·7. $C_5H_7O_3N_2Cl_3$ requires Cl, 42·7%).

γγγ-Trichloro-α-nitro-β-p-toluidinopropane.—25 G. (1 mol.) of γγγ-trichloro-α-nitro-β-acetoxypropane and 22 g. (2 mols.) of *p*-toluidine were dissolved in 100 c.c. of 99·5% alcohol and heated to gentle boiling for 15—20 minutes until most of the alcohol had boiled away. The issuing vapour was distinctly acid from the liberation of acetic acid. The whole was poured into water and the viscid mass obtained was well washed with dilute acetic acid and finally with water and dissolved in hot alcohol. On cooling, *γγγ-trichloro-α-nitro-β-p-toluidinopropane* separated in large yellow compact crystals, readily soluble in warm alcohol or light petroleum, from which it crystallised in aggregates of very pale yellow rhombs, m. p. 61° (Found: Cl, 35·6; N, 9·5. $C_{10}H_{11}O_2N_2Cl_3$ requires Cl, 35·8; N, 9·5%).

γγγ-Trichloro-α-nitro-β-phenylhydrazinopropane.—25 G. (1 mol.) of γγγ-trichloro-α-nitro-β-acetoxypropane and 22 g. (1 mol.) of phenylhydrazine were dissolved in 50 c.c. of 99·5% alcohol and heated to gentle boiling for 10 minutes. *γγγ-Trichloro-α-nitro-β-phenylhydrazinopropane*, which separated on cooling, crystallised from boiling alcohol, in which it was moderately easily soluble, in very pale yellow, six-sided prisms with domed ends, m. p. about 120° (decomp.; rapid heating) (Found: C, 36·4; H, 3·2; N, 14·1; Cl, 35·7. $C_9H_{10}O_2N_3Cl_3$ requires C, 36·2; H, 3·0; N, 14·1; Cl, 35·6%). When heated with acetic anhydride, it formed *γγγ-trichloro-α-nitro-β-diacetylphenylhydrazinopropane*, CCl_3·CH(NAc·NAcPh)·CH_2·NO_2. This crystallised from glacial acetic acid in colourless, six-sided, flattened prisms with domed ends, m. p. 199—200° (decomp.; rapid heating), but the exact m. p. depends on the rate of heating (Found: N, 11·1; Cl, 27·9. $C_{13}H_{14}O_4N_3Cl_3$ requires N, 11·0; Cl, 27·8%).

A nnmber of other hydrazino-derivatives were similarly prepared: *γγγ-trichloro-α-nitro-β-p-tolylhydrazinopropane* crystallised from alcohol in very pale yellow, six-sided prisms with domed ends, m. p. 115° (Found: Cl, 34·1. $C_{10}H_{12}O_2N_3Cl_3$ requires Cl, 34·1%), and its *diacetyl* derivative from acetic acid in thin, colourless, four-sided plates, m. p. 157—158° (Found: Cl, 27·2. $C_{14}H_{16}O_4N_3Cl_3$ requires Cl, 26·9%). *γγγ-Trichloro-α-nitro-β-p-chlorophenylhydrazinopropane* separated from alcohol in very pale yellow, stout, six-sided prisms with domed ends, m. p. 118° (Found: Cl, 42·7. $C_9H_9O_2N_3Cl_4$ requires Cl, 42·6%), and its *diacetyl* derivative from acetic acid, in which it was sparingly soluble, in clusters of small colourless plates, m. p. 152° (Found: Cl, 33·7. $C_{13}H_{13}O_4N_3Cl_4$ requires Cl, 33·6%). *γγγ-Trichloro-α-nitro-β-2:4-dichlorophenylhydrazinopropane* formed very pale yellow needles, m. p. 79°, from alcohol (Found: Cl, 47·7. $C_9H_8O_2N_3Cl_5$ requires Cl, 48·3%), and its *diacetyl* derivative, slender colourless prisms, m. p. 125°, from acetic acid (Found: N, 9·8; Cl, 40·1. $C_{13}H_{12}O_4N_3Cl_5$ requires N, 9·5; Cl, 39·3%). *γγγ-Trichloro-α-nitro-β-m-nitrophenylhydrazinopropane* crystallised from alcohol in bright yellow, rhombic plates, m. p. 112—113° (Found: N, 16·2; Cl, 31·2. $C_9H_9O_4N_4Cl_3$ requires N, 16·3; Cl, 31·0%).

γγδ-Trichloro-α-nitro-β-acetoxypentane reacts with ammonia, amines, and hydrazines in a similar manner to γγγ-trichloro-α-nitro-β-acetoxypropane.

γγδ-Trichloro-α-nitro-β-aminopentane was prepared by saturating a solution of γγδ-trichloro-α-nitro-β-acetoxypentane in absolute alcohol (99·5%) with dry ammonia, isolated as the hydrochloride, and liberated from its mixture with ammonium chloride much as previously described. It crystallised from alcohol in aggregates of colourless plates, m. p. 54—55° (Found: N, 11·7; Cl, 45·3. $C_5H_9O_2N_2Cl_3$ requires N, 11·9; Cl, 45·2%). The very easily soluble *hydrochloride* crystallised from dilute hydrochloric acid in small, colourless, short, six-sided prisms with domed ends (Found: Cl as HCl, 13·1; total Cl, 52·3. $C_5H_9O_2N_2Cl_3$,HCl requires Cl as HCl, 13·1; total Cl, 52·2%). When heated with acetic anhydride, the base formed a well-crystallised *monoacetyl* derivative, which separated from acetic acid in thin, colourless, elongated, transparent plates, m. p. 104° (Found: Cl, 38·6. $C_7H_{11}O_3N_2Cl_3$ requires Cl, 38·4%).

γγδ-Trichloro-α-nitro-β-p-toluidinopentane.—28 G. (1 mol.) of γγδ-trichloro-α-nitro-β-acetoxypentane and 22 g. (2 mols.) of *p*-toluidine were dissolved in 200 c.c. of alcohol (99·5%) and heated to gentle boiling for about ½ hour until the bulk was reduced to half; the mixture was then poured into excess of water. The product was well washed with dilute acetic acid and finally with water. This is necessary to remove the excess of toluidine and any small amount of unchanged ester, as, if these are not removed, subsequent crystallisation is difficult. The viscid mass thus obtained was dissolved in a little hot alcohol and cooled; *γγδ-trichloro-α-*

nitro-β-p-toluidinopentane then separated in short, compact, six-sided, yellow prisms, m. p. 110° (Found: N, 8·8; Cl, 32·4. $C_{12}H_{15}O_2N_2Cl_3$ requires N, 8·6; Cl, 32·7%).

γγδ-Trichloro-α-nitro-β-phenylhydrazinopentane, prepared similarly to the previous compound, crystallised from hot alcohol, in which it was moderately easily soluble, in aggregates of slender, flattened, six-sided prisms, almost colourless with a very faint yellow tint, m. p. 129° (Found: Cl, 32·6. $C_{11}H_{14}O_2N_3Cl_3$ requires Cl, 32·6%). Heated with excess of acetic anhydride, it formed a *monoacetyl* compound, which crystallised from alcohol in six-sided prisms, almost colourless with a very faint yellow tint, m. p. 111° (Found: N, 11·3; Cl, 29·1. $C_{13}H_{16}O_3N_3Cl_3$ requires N, 11·4; Cl, 28·9%). The action of acetic anhydride does not so easily carry the acetylation further, as with γγγ-trichloro-α-nitro-β-phenylhydrazinopropane, for when the monoacetyl compound was dissolved in hot acetic anhydride and cooled, it separated unchanged. When, however, it was heated with acetic anhydride in presence of a drop of concentrated sulphuric acid, the *diacetyl* compound was formed. It crystallised from acetic acid in colourless slender prisms, m. p. 158—159° (Found: Cl, 26·3. $C_{15}H_{18}O_4N_3Cl_3$ requires Cl, 25·9%).

THE QUEEN'S COLLEGE, OXFORD. [*Received, January 15th*, 1936.]

84. *Interaction of Carbon Monoxide and Alcohols. Part II. Synthesis of Propionic and* iso*Butyric Acids.*

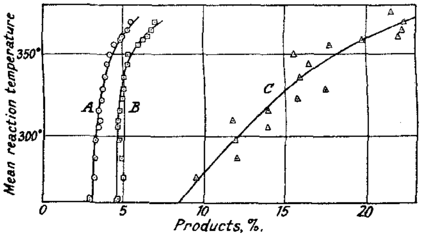
By DOUGLAS V. N. HARDY.

PART I of this series (J., 1934, 1335) was concerned with the synthesis of acetic acid from carbon monoxide and methyl alcohol, a reaction constituting the first stage of Fischer's suggested mechanism (*Ind. Eng. Chem.*, 1925, **17**, 576) for building up carbon chains from carbon monoxide and hydrogen. This communication deals with the second and the third stage of chain elaboration, *viz.*, the conversion of two- and three-carbon alcohols into three- and four-carbon acids respectively:

$$EtOH + CO \longrightarrow Et{\cdot}CO_2H \; ; \; CHMe_2{\cdot}OH + CO \longrightarrow CHMe_2{\cdot}CO_2H$$

Mixtures of alcoholic vapour, steam, and carbon monoxide were passed under a pressure of 200 atm. through phosphoric acid containing a small amount of copper phosphate, a catalyst which had proved efficient for the synthesis of acetic acid (Part I, *loc. cit.*).

FIG. 1.



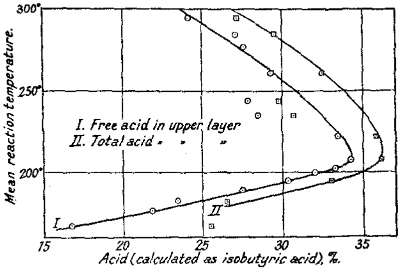
A. Free propionic acid. B. Total propionic acid. C. Ethylenic polymerides.

Between 250° and 370° the product from ethyl alcohol consisted of an upper layer, principally high-boiling polymerides of ethylene, and a lower layer containing water, unchanged alcohol, small amounts of propionic acid and ethyl propionate, and traces of acetaldehyde and volatile hydrocarbons. Fig. 1 illustrates the effect of reaction temperature upon the production of upper layer and propionic acid, both of which are favoured by rise of temperature. It will be seen that ethylenic polymerides were formed at 2—3 times the

rate at which propionic acid was produced, and hence, under these conditions, the synthesis of propionic acid from ethyl alcohol is an inefficient process. It seems likely, however, that employment of much higher pressures, *e.g.*, 500—1000 atm., would give favourable results.

Both *n*- and *iso*-propyl alcohol reacted readily with carbon monoxide at comparatively low temperatures, *e.g.*, 150—250°. Two-layer products were obtained which consisted chiefly of acids, unsaturated hydrocarbons, unchanged alcohol, and water. Fig. 2 shows the variation of free and total acid with reaction temperature in the case of *iso*propyl alcohol, and indicates an optimum at 210—215°. On investigating the acidic constituents of the products from these two alcohols, three significant facts were revealed: (a) *iso*-butyric acid was the chief constituent, (b) *n*-butyric acid was absent, (c) substantial but variable amounts of higher acids were present. It was concluded that the alcohols as such were not implicated in the reaction with carbon monoxide, but were dehydrated to propylene; part of the latter then reacted with steam and carbon monoxide, which, in harmony

FIG. 2.



with the modern conception of its structure (C ⩸ O), was added to the β-carbon atom of propylene, giving *iso*butyric acid:

$$\left.\begin{matrix} CH_3\cdot CH_2\cdot CH_2\cdot OH \\ (CH_3)_2CH\cdot OH \end{matrix}\right\rangle \longrightarrow CH_3\cdot CH{:}CH_2 \xrightarrow{CO+H_2O} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle CH\cdot CO_2H$$

Of the residual propylene, part polymerised, and the remainder was found both in the gaseous phase and dissolved in the liquid product, from which it escaped when the pressure was released. A part of the olefinic hydrocarbons formed by polymerisation of proplyene remained unchanged, and the remainder reacted with steam and carbon monoxide to produce higher acids. In agreement with this view, it was found that the higher acids appeared to be members of the series $C_{3n}H_{6n+1}\cdot CO_2H$.

Examination of the material consisting chiefly of unsaturated hydrocarbons showed the presence of ketones and probably ethers. These constituents were not completely investigated, but methyl *iso*butyl ketone and di*iso*propyl ketone were identified in the product from *iso*propyl alcohol. The presence of these two constituents suggests two different methods of formation, *viz.*, (a) dehydrogenation of higher alcohols formed either by auto-condensation of alcohol or by hydration of a higher olefin:

$$2CHMe_2\cdot OH \xrightarrow{-H_2O} CHMe_2\cdot CH_2\cdot CH(OH)\cdot CH_3 \xleftarrow{+H_2O} CHMe_2\cdot CH{:}CHMe \longleftarrow 2CHMe{:}CH_2$$

$$CHMe_2\cdot CH_2\cdot CH(OH)\cdot CH_3 \longrightarrow CHMe_2\cdot CH_2\cdot COMe + H_2$$

(b) loss of carbon dioxide from two molecules of acid:

$$2CHMe_2\cdot CO_2H \longrightarrow (CHMe_2)_2CO + CO_2$$

The following carbon balances were obtained in experiments which, so far as possible, were carried out in a quantitative manner.

		n-Propyl alcohol.		*iso*Propyl alcohol.	
Carbon introduced	As alcohol	1000		1000	
	As CO	74		75	
		1074		1075	
Carbon accounted for	As unchanged alcohol		429		254
	As acids		397		463
	As liquid hydrocarbons, ketones (and ethers ?)		140		173
	As C_3H_6 in gaseous phase		8		60
		974	974	950	950
	Apparent loss	100		125	

In these experiments the greater part of the apparent loss was due to escape of dissolved propylene when liquid was withdrawn from the high-pressure product receiver. The residual gases contained no products other than propylene. Only 57% of *n*- but 75% of *iso*-propyl alcohol reacted, a comparison which suggests the greater ease of dehydration of the latter. Although in the two cases carbon monoxide reacted substantially to the same extent, the acids from *iso*propyl alcohol contained more carbon, owing to the presence of an increased proportion of higher acids.

EXPERIMENTAL.

Apparatus.—The high-pressure circulatory apparatus described in Part I (*loc. cit.*) was used.

Catalyst.—A mixture of copper phosphate (14 g.) and phosphoric acid (700 g. of 87%) was uniformly employed.

Reaction Conditions.—The working pressure was in all cases 200 atm., and the rate of gas circulation was 40 l. of compressed gas per hour. Generation of alcoholic vapour and steam was accomplished by introducing 80% alcohol into the vaporiser.

Ethyl Alcohol and Carbon Monoxide.—Results summarised in Fig. 1 were obtained by examination of samples taken at intervals of 15 minutes while the reaction temperature was gradually raised from 260° to 380°. The rate of vaporisation was constant throughout, and yielded approximately 160 g. of product per hour. The combined upper layers commenced to boil at about 200°, and 34% distilled between 200° and 300° as a light yellow, unsaturated oil. After neutralisation and hydrolysis with a small excess of sodium hydroxide, the lower layers gave an alcoholic distillate which furnished a small amount of volatile hydrocarbons when diluted, and gave acetaldehyde-2:4-dinitrophenylhydrazone (m. p. 155—157°; mixed m. p. 160—161°) when treated with the hydrazine in presence of acid. The solution of sodium salts was evaporated to dryness, and the residue distilled with concentrated sulphuric acid. Water was removed from the distillate with benzene by the azeotropic method. The resulting acid boiled almost entirely between 135° and 142° and consisted of propionic acid (*p*-phenylphenacyl ester, m. p. 92—95°; mixed m. p. 93—96°).

The Propyl Alcohols and Carbon Monoxide.—The data above refer to experiments in which the reaction temperature was 205—210°, and the following quantities of alcohols were passed through the catalyst during 6½ hours: *n*-propyl alcohol, 1118 g.; *iso*propyl alcohol, 887 g. The products were worked up as follows. After separation of the two layers, the lower was made alkaline and distilled, the alcohol–water azeotrope being obtained. The upper layer was boiled under reflux for 2 hours with a 5% excess of sodium hydroxide solution (50%) and was distilled until all the alcohol and part of the hydrocarbons had passed over. Dilution of the distillate gave an upper layer of hydrocarbons, etc., which was repeatedly washed with water to remove alcohol. Distillation of the aqueous layer and washings gave the alcohol–water azeotrope. Hydrocarbons, etc., were separated from the residual solution of sodium salts and combined with those from the distillate. The combined solutions of sodium salts were evaporated to dryness, and the residue made strongly acid with concentrated hydrochloric acid. After extraction with benzene, the liberated acids were dried azeotropically and distilled.

n-*Propyl alcohol.* The product (above) consisted of 1093 g. of upper layer (C, 56·65; free acid,* 23·9; total acid,* 32·4%) and 282 g. of lower layer (C, 10·4; free acid,* 3·35%). The

* Calculated on the assumption that the molecular weight of the acid was 88.

upper layer (1003 g.) gave 653 g. of distillate (C, 45·3%) from which 64·3 g. of hydrocarbons, etc., (C, 82·9; H, 13·9%) were obtained; non-volatile hydrocarbons, etc. (C, 80·4; H, 12·9%), weighed 40·9 g. The lower layer (242 g.) furnished 47 g. of *n*-propyl alcohol–water azeotrope (71·7% alcohol). The acids (average molecular weight, 108) distilled as follows: < 150° (7·5 g.); 150—159° (126·5 g.); 159—175° (73 g.); residue (73 g.). The anilide of the acid, b. p. 154·5°, had m. p. 101—102° (mixed m. p. with *iso*butyranilide, 102°). The anilide from the acid of b. p. 163—166° showed no resemblance to *n*-butyranilide (m. p. 94°) and melted at 101—102° (mixed m. p. with *iso*butyrauilide, 99—99·5°).

iso*Propyl alcohol.* The product obtained in the quantitative experiment (p. 360) consisted of 726 g. of upper layer (C, 60·15; free acid*, 35·8; total acid,* 38·1%) and 281 g. of lower layer (C, 12·7; free acid,* 5·5%). The upper layer (640 g.) gave an alcoholic distillate (231 g.; C, 54·8%), from which 34·8 g. of hydrocarbons, etc. (C, 84·8; H, 14·5%), were obtained; non-volatile hydrocarbons, etc. (C, 84·5; H, 13·4%), weighed 61 g. The lower layer (242 g.) yielded 43 g. of *iso*propyl alcohol–water azeotrope (87·9% alcohol). Distillation of the acids (average molecular weight = 116) was as follows: 150—159° (131 g.); 159—175° (4 g.); residue (116 g.). The anilide of the acid of b. p. 154·5° melted at 102—102·5° (unchanged on admixture with *iso*butyranilide). The acid of b. p. 163—166° gave an anilide (needles, m. p. 99·5—100·5°) which differed from *n*-butyranilide (rhombs, m. p. 94°) and slightly depressed the m. p. of *iso*butyranilide.

The more complex residual acids were examined as follows. 400 G. of crude acids were boiled under reflux with methyl alcohol (400 g.) and sulphuric acid (24 g.) for 8 hours. The resulting esters were freed from alcohol and acid in the usual manner and fractionally distilled:

B. p.	92—100°	100—130°	130—145°	145—154°	154—170°	Residue
Wt. (g.)	155	14	11	28	10	160

Fraction 1 consisted of methyl *iso*butyrate, and fraction 4 contained a methyl heptoate which, after hydrolysis, yielded a heptoic acid, b. p. 102—106°/14 mm. (*M*, by titration, 130·3. Calc. for $C_7H_{14}O_2$: *M*, 130), whose anilide crystallised from petrol (b. p. 60—80°) in colourless needles, m. p. 68°. The residual esters were distilled further under reduced pressure:

B. p. /15 mm.	Wt. (g.).	Found. C, %.	Found. H, %.	B. p. /15 mm.	Wt. (g.).	Found. C, %.	Found. H, %.
80—90°	27·2	70·2	11·8	140—150°	13·9	70·9	11·9
90—100	24·5	70·9	11·9	150—170	22·0	71·9	11·8
100—110	8·4	70·4	11·9	170—180	7·9	73·5	12·2
110—120	9·0	70·7	11·8	Residue	8·0	—	—
120—140	20·7	71·1	11·7				

Calc. for $C_9H_{19}\cdot CO_2CH_3$: C, 70·9; H, 11·9%. Calc. for $C_{12}H_{25}\cdot CO_2CH_3$: C, 73·6; H, 12·4%.

Material described above as volatile and non-volatile "hydrocarbons, etc.," was fractionally distilled:

B. p.	100—120°	120—135°	135—150°	150—160°	160—170°	170—180°	180—190°	190—200°	200—210°	Residue
Wt. (g.)	7·7	22·2	16·1	14·0	2·9	6·3	14·1	10·0	12·0	32·0

All the fractions were pleasant smelling, and decolorised bromine water. Analyses gave the following results:

B. p. of fraction	120—135°	180—190°	200—210°
C, %	81·9	83·3	84·1
H, %	14·2	13·7	13·6

Failure to react with metallic sodium showed the absence of higher alcohols. Treatment of an alcoholic solution of fraction, b. p. 100—120°, with 2 : 4-dinitrophenylhydrazine in presence of a few drops of concentrated hydrochloric acid gave orange crystals which, after recrystallisation from light petroleum (b. p. 60—80°), melted at 90—91° alone or mixed with methyl *iso*butyl ketone 2 : 4-dinitrophenylhydrazone. Similarly, the fraction, b. p. 120—135°, gave yellow crystals which, after recrystallisation, had m. p. 88—89°, raised to 92—93° on admixture with di*iso*propyl ketone 2 : 4-dinitrophenylhydrazone (m. p. 94—98°). After complete removal of ketone with 2 : 4-dinitrophenylhydrazine, the fraction of b. p. 120—135° was recovered and distilled. The portion, b. p. 120—135°, still contained oxygen (Found: C, 83·8; H, 14·5%).

Data for Fig. 2 (p. 359) were obtained by examination of samples taken at intervals of 15 minutes while the reaction temperature was slowly increased from 160° to 300°. The rate of collection of product was 180—200 g. per hour. The following table gives further relevant data:

Mean reaction temp.	167°	182°	195°	208°	222°	235°	244°	261°	277°	285°	295°
Acid, %, in lower layer *	4·2	4·1	4·5	5·0	5·5	6·0	6·5	6·9	6·8	6·5	6·2
$\frac{\text{Wt. of upper layer}}{\text{Wt. of lower layer}}$	3·1	2·1	1·9	2·3	1·7	1·3	1·2	0·9	0·6	0·5	0·4

CHEMICAL RESEARCH LABORATORY, TEDDINGTON. [*Received, February 5th*, 1936.]

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85. *Interaction of Carbon Monoxide and Alcohols. Part III. Synthesis of Methylethylacetic and Pivalic Acids.*

By DOUGLAS V. N. HARDY.

UNDER conditions identical with those employed in Part II (preceding paper), the reactions between carbon monoxide and *n*-, *sec.*-, and *iso*-butyl alcohols have now been examined. In each case, formation of acids took place most readily at 200—210°. The products, which closely resembled those from the propyl alcohols, consisted of an upper layer containing unchanged alcohol, acids, esters, and hydrocarbons, and a lower aqueous layer in which small amounts of acids and unchanged alcohol were dissolved.

The acids from *n*- and *sec.*-butyl alcohol were methylethylacetic and pivalic (trimethylacetic), with a considerable proportion of higher homologues, of which nonoic acids were the chief constituents. The separation of methylethylacetic from pivalic acid could only be accomplished after conversion into their methyl esters, whereby it was found that pivalic acid was the major component. On the other hand, *iso*butyl alcohol yielded pivalic and higher acids with but a trace of methylethylacetic acid, so that almost pure pivalic acid was obtainable by fractional distillation.

As suggested in Part II (*loc. cit.*), it is again evident that the alcohols are converted into butylenes and butylenic polymerides. With carbon monoxide and steam the former yield five-carbon acids whereas the latter lead to higher acids. The molecular rearrangements involved in converting *n*- and *sec.*-butyl alcohol into pivalic acid, and *iso*butyl alcohol into methylethylacetic acid must be attributed to butylenic interchange, evidence for which has been provided by Konovalov (*Ber.*, 1880, **13**, 2395), Ipatiev (*Ber.*, 1903, **36**, 1999; 1907, **40**, 1827), Senderens (*Compt. rend.*, 1907, **144**, 1110), and others:

$$CH_2Et{\cdot}CH_2{\cdot}OH \longrightarrow CHEt{:}CH_2 \xrightarrow{CO+H_2O} CHMeEt{\cdot}CO_2H$$
$$\updownarrow$$
$$CHMeEt{\cdot}OH \longrightarrow CHMe{:}CHMe \xrightarrow{CO+H_2O} CHMeEt{\cdot}CO_2H$$
$$\updownarrow$$
$$CHMe_2{\cdot}CH_2{\cdot}OH \longrightarrow CMe_2{:}CH_2 \xrightarrow{CO+H_2O} CMe_3{\cdot}CO_2H$$

Young and Lucas (*J. Amer. Chem. Soc.*, 1930, **52**, 1964) consider that *iso*butylene is not obtainable from α- and β-butanol by catalytic dehydration, but under the experimental conditions employed in this research it is evident that, not only is their view incorrect, but *iso*butylene must be the chief dehydration product.

It was always observed that, after use, the catalyst contained metallic copper, evidently produced by reduction of the initial copper phosphate. Since the efficiency was unimpaired, it appeared that copper phosphate might have no promoting action in these experiments. To test this matter, phosphoric acid alone was employed as catalyst in an experiment with *n*-butyl alcohol and carbon monoxide; formation of acids occurred quite readily, and the product was indistinguishable from others obtained by the employment of copper-containing catalysts.

The following carbon balance was obtained :

Carbon introduced, g.		Carbon accounted for, g.	
As *n*-butanol	1000	As unchanged *n*-butanol	437
,, CO	62·5	,, hydrocarbons, etc.	97
		,, acids	437·5
	1062·5	,, butylenes	55·5
		Loss	35·5
			1062·5

Experimental.

Except where otherwise mentioned, the experimental conditions and the method of working up the products were as described in Part II. The alcohols were introduced into the vaporiser after addition of 25% by weight of water. Conversion of methyl esters into the corresponding anilides was accomplished by treatment with anilinomagnesium bromide (Hardy, this vol., p. 398).

n-*Butyl Alcohol and Carbon Monoxide*.—(1) *Copper phosphate–phosphoric acid catalyst*. After approx. 2400 g. of *n*-butyl alcohol had been passed through the catalyst at 205—210° during 13 hours, the product, which contained 2243 g. of upper layer (free acid,* 23·2; total acid,* 26·3%) and 380 g. of lower layer (free acid,* 1·6%), furnished 1160 g. of dry butyl alcohol and 115 g. of hydrocarbons, etc. The acids distilled as follows :

B. p.	160—169°	169—190°	Residue	Total
Wt. (g.)	304	84	190	578

Fractions 1 and 2 were separately converted into methyl esters, and those from the first fraction were fractionally distilled up to 110°, whereupon esters from the second were added and distillation continued :

B. p.	99—104°	104—108·5°	108·5—113°	113—125°	Residue
Wt. (g.)	245	37·5	1·5	80	19·5

Fraction 1 consisted of methyl pivalate and gave pivalanilide, m. p. 125—125·5° and mixed m. p. with an authentic specimen (m. p. 131°) 126—129°. Fraction 4 was methyl methylethylacetate, and a portion, b. p. 114—117°, gave an anilide, m. p. 103—106°, mixed m. p. with methylethylacetanilide (m. p. 107—108°) 104—107°.

(2) *Phosphoric acid catalyst*. In 6 hours, 749 g. of *n*-butanol were passed through the catalyst at 204—207° ; the upper layer of product (C, 58·8 ; free acid,* 28·9 ; total acid,* 32·9%) weighed 788 g., and the lower layer (C, 4·5 ; free acid,* 1·8%) 218 g. From the upper layer (704 g.) were obtained 48·5 g. of hydrocarbons, etc. (C, 78·2 ; H, 13·0%), and aqueous butanol equivalent, from its carbon content, to 294 g. of dry alcohol. A further quantity (8 g.) of *n*-butyl alcohol was obtained from the lower layer (91 g.). The approximate distribution of the acids was shown by distillation :

B. p.	159—170°	170—190°	Residue	Total
Wt. (g.)	115	22·5	99·5	237

A quantity of residual acids (b. p. > 190°) was distilled up to 130°/2 mm. and then further to 143°/2 mm., whereupon decomposition commenced. The portion, b. p. < 130°/2 mm., was redistilled under atmospheric pressure with an electrically-heated Dufton column, and the equivalent weights of the fractions were determined by titration (Calc. for $C_8H_{17}\cdot CO_2H$: *M*, 158).

B. p.	183—190°	190—200°	200—210°	210—220°	220—230°	230—240°	240—270°	Residue 2	130—143°/2 mm.	Residue 1
Wt., %	9·3	4·3	8·3	6·4	4·7	31·6	13·2	5·1	7·0	10·0
M	113·5	120	135	150	159	158	177	—	245	—

sec.-*Butyl Alcohol and Carbon Monoxide*.—Passage of *sec*.-butyl alcohol (*ca*. 1 kg.) through the catalyst at 200—210° during 6½ hours gave 819 g. of upper layer (Free acid,* 37·3; total acid,* 44·3%) and 333 g. of lower layer (Free acid,* 3·2%). The upper layer (740 g.) contained 214 g. of unchanged alcohol and 46 g. of hydrocarbons, etc. Unchanged alcohol (15 g.) was also obtained from the lower layer (298 g.). The acids were distilled as follows : (1) 160—170°,

* Calculated on the assumption that its molecular weight is 102.

67·4 g.; (2) 170—190°, 105·3 g.; residue, 105 g.; and the methyl esters from (1) and (2) were then fractionally distilled :

B. p.	98—104°	104—109°	109—114°	114—118°	Residue
Wt., %	28·8	19·9	17·4	10·5	23·4

The ester of b. p. 99—102° gave an anilide (m. p. 124—126°; mixed m. p. with pivalanilide, 127—129°), and that of b. p. 114—118° gave methylethylacetanilide (m. p. 104—105°; mixed m. p. 105—106°).

*iso*Butyl *Alcohol and Carbon Monoxide.*—*iso*Butyl alcohol (*ca.* 1 kg.) was passed through the catalyst at 215—216° in 6 hours, and produced 1070 g. of upper layer (free acid,* 22·7; total acid,* 26·4%) and 234 g. of lower layer (free acid,* 1·6%). The product (986 g. of upper, and 214 g. of lower layer) gave dry *iso*butyl alcohol (416 g.) and hydrocarbons, etc. (52 g.). Acids were fractionally distilled : (1) 160—164°, 23 g.; (2) 164—166°, 102 g.; (3) 166—180°, 28 g.; (4) residue, 69 g. Fraction (2) solidified and consisted of fairly pure pivalic acid (anilide, m. p. 124—125°; mixed m. p. 125—129°), which melted at 28—30° after drainage in a sintered-glass funnel under reduced pressure. Fractions (1) and (2) were united and converted into methyl esters, which were fractionally distilled :

B. p.	99—104°	104—109°	109—114°	114—118°	Residue
Wt., %	61·4	20·2	4·5	3·1	10·8

The ester of b. p. 114—118° gave an anilide (m. p. 94—95°; mixed m. p. with methylethylacetanilide, 95—98°).

The author gratefully acknowledges the assistance of Mr. D. G. Grant in the work described in this and the preceding paper.

Chemical Research Laboratory, Teddington. [*Received, February 5th*, 1936.]

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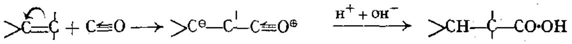
86. *Interaction of Olefins, Carbon Monoxide, and Steam.*

By Douglas V. N. Hardy.

The experiments described in the two preceding papers have furnished evidence which strongly suggests that, under high pressure and in presence of acidic catalysts, olefins are capable of uniting with carbon monoxide and steam to give acids (cf. U.S.P. 1,924,762—8, 1,957,939). This hypothesis has now been confirmed with ethylene, propylene, and Δ^{β}-butylene. Passage of a mixture of the first with carbon monoxide and steam through phosphoric acid caused slow formation of propionic acid, but ethyl alcohol and ethylenic polymerides were also produced. Under 150 atm. and at 290—300°, it was found that, for every molecule of ethylene converted into acid, approximately three were hydrated and two polymerised, a position which recalls the difficnlties encountered in the conversion of ethyl alcohol into propionic acid (Hardy, this vol., p. 358). Treatment of propylene and Δ^{β}-butylene at 200° and 200 atms. caused fairly rapid formation of liquid products, which contained a large proportion of acids, together with hydrocarbons. As was indicated in the collateral experiments with the alcohols (two preceding papers), propylene gave a mixture of *iso*butyric acid and homologues, and Δ^{β}-butylene produced pivalic, methylethylacetic, and higher acids.

Formation of acids from olefins, steam, and carbon monoxide must be due primarily to activation of the olefin molecule, which is then able to unite with carbon monoxide, reaction being completed by addition of the elements of water :



When phosphoric acid is used as catalyst, activation doubtless occurs by formation and subsequent decomposition of alkyl phosphates.

EXPERIMENTAL.

Apparatus.—The high-pressure circulatory apparatus (Hardy, J., 1934, 1339) was employed, but for the experiments with propylene and Δ^{β}-butylene the force-pump was disconnected from the vaporiser. The latter contained an initial charge of water, and the liquid hydrocarbons were withdrawn from inverted cylinders by means of the force-pump and delivered into the apparatus at a point in front of the first preheater.

Materials.—Propylene was prepared from *iso*propyl alcohol (Senderens, *Compt. rend.*, 1910, **151**, 394 ; *Bull. Soc. chim.*, 1911, **9**, 373) obtained by catalytic hydrogenation of acetone. By means of a Geryk pump it was compressed into a cylinder cooled to − 20°. Δ^{β}-Butylene was obtained from *n*-butyl alcohol and 60% sulphuric acid (Young and Lucas, *J. Amer. Chem. Soc.*, 1930, **52**, 1964) and was liquefied by cooling to − 20°.

Ethylene, Carbon Monoxide, and Steam.—A mixture of ethylene (1 vol.) and carbon monoxide (4 vols.) under a pressure of 150 atm. was circulated at a rate of 40 l. of compressed gas per hour through phosphoric acid (350 g. of 87%) at 290—300°. The product (500 g.) contained an upper layer (16·5 g.) of high-boiling hydrocarbons, and a lower, aqueous layer (acidity, 0·5*N*). After neutralisation with sodium hydroxide solution, the latter gave an alcoholic distillate equivalent to 37 g. of ethyl alcohol, and a residual solution of sodium salts, which was concentrated and treated with *p*-phenylphenacyl bromide; *p*-phenylphenacyl propionate (m. p. 95—97°; mixed m. p. 97—99°) was obtained.

Propylene, Carbon Monoxide, and Steam.—Carbon monoxide under 200 atms. was led (40 l. of compressed gas per hour) through phosphoric acid (700 g. of 87%) at 200°, and, the water-vaporiser being maintained at 100°, propylene (850 g.) was regularly injected during 6 hours. The product, which consisted of 546 g. of upper layer (free acid,* 41·5 ; total acid,* 50·8%) and 284 g. of lower layer (free acid,* 6·2%), was boiled under reflux with sodium hydroxide solution (110 g. in 250 c.c.) for 2 hours, and was then distilled until only water was passing over. Repeated washing of the upper layer of distillate with water gave 88·4 g. of hydrocarbons, etc., and distillation of the washings gave a small amount of aqueous *iso*propyl alcohol (equivalent to 3 g. of alcohol). Non-volatile hydrocarbons, etc. (61·3 g.), were separated from the residue which, after concentration, was strongly acidified with concentrated hydrochloric acid. The liberated acids were extracted with benzene, dried by the azeotropic method, and distilled : < 150° (1·7 g.), 150—159° (105·0 g.), 159—175° (14·1 g.), residue (173 g.). A portion of acid, b. p. 154—155°, gave an anilide, m. p. and mixed m. p. with *iso*butyranilide 102·5—103°. The absence of *n*-butyric acid was shown by converting a portion of acid of b. p. 163—164° into its anilide, which formed needles, m. p. 100—101·5° (*n*-butyranilide crystallises in rhombs, m. p. 94°). Admixture with *iso*butyranilide depressed the m. p. to 98—98·5°.

Δ^{β}-Butylene, Carbon Monoxide, and Steam.—Under conditions described in the foregoing experiment, Δ^{β}-butylene (640 g.) gave a product consisting of upper layer (110 g.; free acid,† 66·4%) and lower layer (528 g.; free acid,† 7·0%), from which hydrocarbons, etc. (10·6 g.), and acids were similarly isolated. The latter were distilled as follows : 160—168° (32·5 g.), 168—190° (23·1 g.), and residue (24·2 g.), and the two fractions of the distillate were separately converted into methyl esters, which were fractionally distilled through a 2′ 6″ Dufton column fitted with a dephlegmator. The combined fractions were as follows : 99—104° (32·8%), 104—109·5° (26·5%), 109·5—114° (13·5%), 114—118° (22·6%), residue (4·6%). Fraction 1 consisted of methyl pivalate, and on treatment with anilinomagnesium bromide (Hardy, this vol., p. 398) gave pivalanilide, m. p. 125—126° and mixed m. p. 127—128°. Fraction 4 contained methyl methylethylacetate, and in like manner gave methylethylacetanilide, m. p. and mixed m. p. 107—108°.

The author thanks Professor G. T. Morgan, Director of Chemical Research, both for helpful criticism and for permission to publish the results in this and the two preceding papers.

CHEMICAL RESEARCH LABORATORY, TEDDINGTON. [*Received, February 5th*, 1936.]

* Calculated on the assumption that the molecular weight of acid is 88.

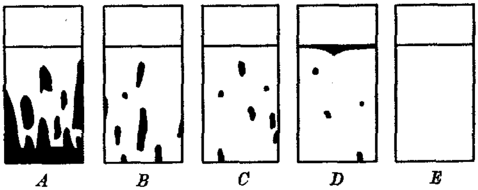
† Calculated on the assumption that the molecular weight is 102.

87. *Some Aspects of the Modern Theories of Corrosion. Part I. Water-line Corrosion.*

By J. E. O. MAYNE.

THE distribution of corrosion on steel plates partly immersed in *N*/10-potassium chloride solution was investigated by Evans and his co-workers, who attributed the corrosion to " electric currents set up by differences in the liquid, notably differences in oxygen concentration, which cause the aerated part of the metal to be cathodic and the unaerated parts to be anodic " (*Proc. Roy. Soc.*, 1931, *A*, **131**, 355). Later (*ibid.*, **1932**, **137**, **345**), they showed that this mechanism gives rise to a protected band along and below the water-line, which, in the centre of the specimen, extends for some distance downwards. If, however, a small quantity of sodium carbonate is added to the chloride solution, severe corrosion may take place at the water-line (see Fig. 1, taken from Evans, " Corrosion of Metals," 1926, p. 114). This local attack cannot be directly explained by the principle of differential aeration, and in order to account for it, Evans has pointed out that under certain conditions the protective films on the metal may fail, forming a " box " with a flap floating on the surface; differential aeration can be set up inside this box, giving rise to water-line attack. The reason for the failure of the film is not clearly explained, however.

FIG. 1.



Effect on the corrosion of steel produced by adding increasing quantities of sodium carbonate to a chloride solution (Evans).

Bengough and Wormwell (*ibid.*, 1933, **140**, 408), on the other hand, attribute water-line attack to " the breakdown of the protective film by wetting and drying and by the action of carbon dioxide and other acid gases in the atmosphere." Hedges (J., 1926, 831) observed water-line attack when magnesium, zinc, and alnminium were attacked by various acids, even in an atmosphere of hydrogen. He therefore concluded that it was due, not to the action of oxygen, but to an enhanced reactivity of the solvent at the surface. This is in accordance with the conclusions of Spring (*Z. physikal. Chem.*, 1889, **4**, 658), who observed the same effect when calcite was dissolved in dilute hydrochloric acid.

In all the above examples, attack has taken place at the surface simultaneously with attack on the rest of the specimen. In order to discover if a type of attack existed which occurred only at the surface of the solution, the distribution of corrosion on steel plates partly immersed in a number of neutral solutions in a vacuum was examined.

EXPERIMENTAL.

The apparatus consisted of a vacuum desiccator, in which was placed a 400-c.c. beaker to contain the solution under examination. The steel specimens, measuring 8 × 5 × 0·04 cm. and cut from annealed mild-steel plate, were polished with No. 1 emery, degreased with carbon tetrachloride, and stored in a desiccator over calcium chloride until required; they were then suspended in the solution by means of a glass hook hanging from a glass rod. The desiccator was evacuated by means of a Hyvac pump, and it was necessary to place air-free water in the desiccator outside the beaker, in order to prevent the surface of the solution from being disturbed by bubbles rising when the pressure became low.

The solutions were rendered air-free by about 10 minutes' boiling in a flask with a narrow

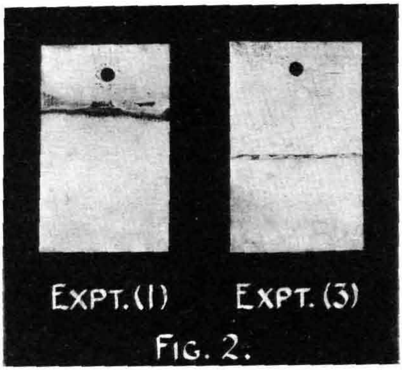


FIG. 2.

[*To face p.* 367.

outlet tube; this tube was then sealed, the flask allowed to cool, the seal broken, and the solution rapidly poured into the beaker. A small manometer was placed inside the desiccator to detect leaks. Each specimen was partly immersed in each solution in a vacuum for one week.

In $N/10$-potassium chloride, at the end of a week, corrosion had occurred along the water-line, and a dark green product had been formed [see Fig. 2, Expt.(1)]; the rest of the plate was only slightly tarnished, doubtless owing to a trace of oxygen in the solution. This is in accordance with the fact that the solution turned slightly brown during the first day of the experiment, but subsequently did not appear to change. At the end of the experiment, the solution contained ferric iron, and after standing in the air for some time, it became much browner. If, during the experiment, air leaked into the desiccator, a small quantity of black corrosion product was formed at the water-line, and below this the plate became evenly corroded; if more air leaked in, water-line attack disappeared altogether, and the distribution of corrosion was in accordance with the work of Evans on partly immersed plates under normal conditions. Steel partly immersed in distilled water under these conditions gave no signs of corrosion after 1 week's immersion.

The effect of a number of different solutions ($N/10$) was next examined. Potassium bromide, iodide, nitrate, or sulphate gave rise to water-line corrosion, but potassium chlorate, hydroxide, carbonate, or chromate, or disodium hydrogen phosphate did not.

In $N/1000$-solution, potassium chloride gave no perceptible corrosion at the water-line, but in $N/100$-solution it gave a fine line of corrosion product.

The effect of addition of ethyl alcohol to the solution was also examined, the following experiments being conducted simultaneously on steel plates: (1) in $N/10$-potassium chloride; (2) in aqueous alcohol of a concentration (mol.-fraction of alcohol = 0·2) at which the curve showing adsorption of alcohol at the surface of the water attains a maximum (Rideal and Schofield, *Proc. Roy. Soc.*, 1925, *A*, **109**, 61); (3) in a solution of the same aqueous alcohol which was also $N/10$ with respect to potassium chloride. In (1), considerable corrosion took place; in (2), a slight dark discoloration appeared at the water-line; and in (3), slight water-line corrosion took place, but considerably less than in (1) (see Fig. 2).

Discussion.

Water-line corrosion is a chemical process, and for this reason only examples in which chemical attack has taken place have been quoted in the introduction. Results obtained by Klobukow (*Z. physikal. Chem.*, 1890, **5**, 180), Beckhold (*ibid.*, 1890, **5**, 68), and Gurwitsch (*ibid.*, 1924, **109**, 375) have been neglected, as they refer to physical solution, and this phenomenon has not been investigated in this paper.

It has been shown that iron immersed in $N/10$-potassium chloride in a vacuum is converted at the water-line into ferrous hydroxide, a reaction which does not take place if the iron is completely immersed under the same conditions. In order to explain this reaction it is necessary to postulate the existence of an electric current. Now, Frumkin (*ibid.*, 1924, **109**, 34) has shown that a potential exists at the surface of a number of electrolytes in water, and this affords a feasible explanation of the above examples of water-line attack. In the cases of chemical surface attack recorded by Spring and by Hedges (*locc. cit.*), the surface of the solution was disturbed by bubbles, and it is suggested that it was the potential which existed in the surface of these bubbles, together with that at the free surface of the solution, which gave rise to the observed phenomenon. This will also account for Spring's observation that when carbon dioxide, air, or hydrogen is allowed to impinge on a calcite crystal immersed in dilute hydrochloric acid, perforation of the crystal takes place at the point of impingement.

The effect of the potential when imposed upon the steel specimen in presence of potassium chloride, bromide, iodide, or sulphate solution would be the production of a soluble ferrous salt, together with potassium hydroxide. The latter would react with the ferrous salt, yielding the green corrosion product observed. It is unfortunate that a trace of air was always present in the solution during these experiments, as this prevented any accurate measurements of the amount of corrosion which had taken place. It cannot be argued, however, that the corrosion observed at the water-line was due to this trace of oxygen, for no corrosion was observed when distilled water was used. Also, since it is easier to pump air out of a desiccator than to remove it from a solution, this trace of oxygen would be in the

solution, and the depolarising action of the oxygen would be uniform all over the plate. Further evidence is to be found in the results of Evans and Borgmann (*Z. physikal. Chem.*, 1932, **160**, 197), who obtained a green corrosion product at the water-line on steel plates partly immersed for 2 days in oxygen-free potassium chloride solution in atmospheres of hydrogen and nitrogen. Now, if a solution of potassium chlorate, hydroxide, carbonate, chromate, or disodium hydrogen phosphate is added to one of a ferrous salt, an insoluble precipitate is formed. The action of the potential at the surface, therefore, would result in the production of an invisible film on the metal as a primary product which would prevent visible corrosion. Experiments were performed with a mixed solution *N*/10 with respect to both potassium chloride and potassium hydroxide, but the results were erratic : sometimes very slight corrosion took place at the water-line, and at other times it was completely inhibited.

The question now arises as to why water-line corrosion does not take place on partly immersed steel plates under normal conditions. Evans (*ibid.*, 1932) has shown that one of the first results of corrosion of steel so immersed in potassium chloride solution under normal conditions is the production of potassium hydroxide just below the surface of the solution. This alkali would prevent attack at the water-line. Water-line corrosion in a chloride solution in the presence of sodium carbonate (as in Fig. 1) can, however, be accounted for similarly. In these experiments we have two sources of alkali which are capable of inhibiting corrosion at the water-line : (1) the added sodium carbonate, which increases from A to E; (2) the alkali formed during the corrosion process, which is proportional to the amount of corrosion which has taken place and clearly decreases from A to E. The specimen D, then, is the one in which the sodium carbonate added to the solution is insufficient to prevent water-line attack, but sufficient to inhibit corrosion of the normal type.

The experiment showing the prevention of water-line attack by the addition of alcohol to the solution is in accordance with the work of Ganguly and Banerji (*Z. anorg. Chem.*, 1922, **124**, 140), who considered that the enhanced reactivity of the solvent at the surface was related to the surface tension of the liquid. This indicates that the attack is related to adsorption of the solute at the surface of the solvent, which takes place in accordance with the Gibbs equation.

SUMMARY.

When a specimen of steel is partly immersed in a de-aerated *N*/10-solution of potassium chloride in a vacuum, attack takes place at the water-line. This is not explained by the present theories of water-line corrosion. It is suggested that it is due to the potential existing at the surface of the solution. Since this water-line attack is depressed by the presence of ethyl alcohol in the solution, it is suggested that it is connected with the negative adsorption of the solute at the surface of the solvent.

This investigation has been carried out as part of the work of the Wire Ropes Research Committee of the Safety in Mines Research Board. The author is indebted to Sir Harold Carpenter for the facilities afforded, and to the Chairman of the board for permission to publish the results. He also thanks Dr. Bengough and Dr. Wormwell for their helpful criticism and interest.

ROYAL SCHOOL OF MINES, S.W. 7. [*Received, December* 16*th*, 1935.]

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88. *The Oxidation of Cyclic Compounds by Potassium Permanganate.*

By C. N. HINSHELWOOD and C. A. WINKLER.

WIDELY different rates are observed for the oxidation of various phenols with potassium permanganate, under conditions where kinetic experiments indicate that the rate-determining process is the initial rupture of the ring (Hinshelwood, J., 1919, **115**, 1180). Except for picric acid (Musgrave and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1933, **29**, 1162), the energies of activation have not hitherto been determined. In order to obtain information

about the probability factor P in the expression, rate $= PZe^{-E/RT}$, the temperature coefficients have now been determined for a series of such oxidation reactions.

5 C.c. of N/10-potassium permanganate solution and 5 c.c. of a solution of the organic compound in dilute sulphuric acid (usually 0·02N) were sealed in glass tubes and allowed to react for measured periods of time. The reaction was stopped by emptying the contents of the tube into potassium iodide solution. Oxides of manganese are precipitated during the reaction and adhere to the sides of the tube, but can be removed by potassium iodide acidified with sulphuric acid. The iodine liberated was titrated with sodium thiosulphate.

Under the conditions of the experiments, the permanganate had only three-fifths of its nominal oxidising power, so the concentration of each solution to be oxidised was chosen so as to be just sufficient for reaction with an equal volume of the permanganate; *i.e.*, the concentration was $0{\cdot}03m/n$ g./l., where n = number of atoms of oxygen required for the complete oxidation of 1 g.-mol. to carbon dioxide, water, and, in the case of nitro-compounds, nitric acid, and m is the molecular weight. (In all cases the complete oxidation occurred more rapidly than the initial step.)

All the organic compounds were recrystallised to constant m. p., thermometers were compared with N.P.L. standards, and blank experiments were made to show that the amount of decomposition which potassium permanganate undergoes by itself under the conditions of the experiments was negligible.

The rate of reaction in most cases can be expressed by the equation $dx/dt = k(a - x)(b - cx)$, where a and b are the initial concentrations of the organic compound and of the permanganate respectively, both in *g.-mols. per l.*, and c is the number of mols. of permanganate used in completely oxidising 1 mol. of the organic compound. With the above concentrations, $a = b/c$; hence $dx/dt = kc(a - x)^2 = k_0(a - x)^2$, and k_0 can be calculated from the percentage change and the time. If, however, we assume that the primary process is a collision between a permanganate ion and a molecule of the organic compound, then we must, for any calculations of molecular statistics, use k, which is given by

$$k_0 \times \text{(concn. of organic substance)/(concn. of permanganate)}$$

When mixed with the other reactant, the permanganate was 0·05N, *i.e.*, M/100, so that

$$k = k_0 \times \text{(concn. of organic substance)} \times 100.$$

With most of the compounds used, the bimolecular formula is fairly well satisfied, though in some cases a trend appears. Three examples are given in Table I. There is no induction period, nor, in general, any autocatalysis which wonld suggest complex mechanisms analogous to those found in the reaction between potassium permanganate and oxalic acid.

TABLE I.

(k is expressed in g.-mol./l./sec.)

Picric acid; 25°. $a = 1{\cdot}07 \times 10^{-3}$.			*m*-Dinitrobenzene; 60°. $a = 1{\cdot}00 \times 10^{-3}$.			Benzoic acid; 60°. $a = 1{\cdot}00 \times 10^{-3}$.		
Mins.	Change, %.	$k \times 10^3$.	Mins.	Change, %.	$k \times 10^3$.	Mins.	Change, %.	$k \times 10^3$.
16	11·2	1·31	60	20·4	7·1	92	10·6	2·1
46	26·9	1·33	126	35·0	7·1	247	18·8	1·6
71	36·2	1·33	241	51·0	7·2	400	28·8	1·7
92	40·6	1·24	363	61·2	7·2	824	44·4	1·6
144	50·8	1·19	432	66·2	7·5	837	45·0	1·6
						1347	59·4	1·8
						1913	67·5	1·8

For the two dinitrophenols, the formula does not hold, but a slight autocatalytic effect appears. Values of k for the primary interaction were calculated from the initial rates, which fortunately could be determined quite accurately, since the reaction–time curves for the two compounds are nearly linear over the first third of their course.

Table II gives the constants at various temperatures, and Table III the values of the activation energies, and of log ($k_{100°} \times 10^7$), $k_{100°}$ being the calculated value of k at 100°.

DISCUSSION.

Before any attempt is made to correlate log k and E, we must consider what agent is responsible for the oxidation. The simplest assumption is that the primary ring-breaking step is an interaction of a permanganate ion with a molecule of the organic compound.

TABLE II.

Picric acid.		2 : 4 : 6-Trinitro-*m*-cresol.		2 : 4-Dinitrophenol.		2 : 6-Dinitrophenol.	
t.	$k \times 10^3$.	t.	$k \times 10^3$.	t.	$k \times 10^3$.	t.	$k \times 10^3$.
15·0°	6·4	25·0°	1·58	0·0°	0·50	0·0°	10·5
25·0	12·8	40·0	5·06	15·6	2·12	15·6	49·6
40·0	35·8	60·0	19·2	25·0	5·06	25·0	119
60·0	115	80·4	82	40·0	18·5	40·0	417

Benzoic acid.		*m*-Dinitrobenzene.		2 : 4 : 6-Trinitro-3-methylnitroaminophenol.	
t.	$k \times 10^4$.	t.	$k \times 10^5$.	t.	$k \times 10^4$.
25·0°	1·97	25·0°	7·71	25·0°	8·3
40·0	5·54	40·0	31·2	40·0	25·8
60·0	17·9	60·0	167	60·0	89
80·0	58·3	80·0	717	80·4	282

TABLE III.

	E.	$\log_{10} (k_{100^\circ} \times 10^7)$.
Picric acid	12,200 *	6·90
Benzoic acid	12,700	5·15
2 : 4 : 6-Trinitro-3-methylnitroaminophenol	13,100	5·90
Trinitro-*m*-cresol	14,600	6·36
2 : 4-Dinitrophenol	15,300	6·98
2 : 6-Dinitrophenol	15,600	8·41
m-Dinitrobenzene	17,300	5·42

* For picric acid, Musgrave and Moelwyn-Hughes (*loc. cit.*) found 12,350 cals.

This is followed by faster reactions which lead to the complete oxidation of the products of ring breaking.* It is difficult to explain the apparently simple second-order course of most of the reactions on any other basis. We must also answer the question whether the organic compounds react as molecules or ions. Since picric acid, trinitrocresol, and 2 : 4 : 6-trinitro-3-methylnitroaminophenol are almost completely ionised in aqueous solution, and since it has been shown that the rate of reaction of picric acid is almost independent of the acidity of the solution, there can be little doubt that the ions themselves react. *m*-Dinitrobenzene does not ionise, and must therefore react as molecules.

Special experiments were made to determine whether benzoic acid and the dinitrophenols react as molecules or ions. The rate of reaction was measured in solutions of sulphuric acid of 0·05, 0·02, and 0·01N concentration. For benzoic acid and 2 : 4-dinitrophenol the rates in the first two solutions were the same, but that in the third was slightly smaller. Hence, it follows that the molecules are the main reacting species, and since, in determining the activation energy, the acid concentration was such that the reaction rate had attained its limiting value, we may use the bulk concentration as that of the reacting species without any correction for change of ionisation with temperature. With 2 : 6-dinitrophenol the situation is not quite so satisfactory : the rate of oxidation increased with increasing sulphuric acid concentration up to $N/10$. This means that molecules rather than ions react, but it also means that a small correction should be applied for change of degree of ionisation with temperature. On the other hand, the small correction would probably not very seriously affect the value 15,600 cals. for the activation energy.

When $\log k$ is plotted against E, a considerable variation in the P values becomes evident, and the influence of the structure of the organic compound on P appears as a very specific one.

Since these results are included in a general statistical survey of bimolecular reactions in the following paper, no further comments need be made here.

SUMMARY.

The activation energies for the oxidation of a number of cyclic compounds by potassium permanganate have been determined for use in a statistical survey of bimolecular reactions.

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* In the two cases where there is an apparent autocatalysis it is probably to be attributed to an inadequate velocity of the reactions succeeding the ring rupture.

89. *On Bimolecular Reactions in Solution.*

By C. N. Hinshelwood and C. A. Winkler.

To a high degree of approximation, the rate of chemical reactions is represented by the Arrhenius equation, which, for our present purpose, is best written in the form : number of molecules reacting $= PZe^{-E/RT}$, Z being the collision number, and P a factor independent of temperature. The interpretation of P has been the subject of much experiment and theory. The study of gas reactions revealed the existence of a considerable number of cases where P approaches unity, thus providing a form of behaviour where activation is not only necessary but also sufficient for reaction. The mechanism of the first-order decomposition of complex organic molecules is, however, much less simple, and factors other than the communication of activation energy play an important part. The same is true of some bimolecular association reactions in gases, and, especially, of many bimolecular reactions in solution, which tend, on the whole, to involve considerably more complex structures than most of those concerned in second-order reactions accessible to measurement in the gaseous state.

Attention was first directed by Christiansen (*Z. physikal. Chem.*, 1924, **113**, 35) to the fact that for these solution reactions P may be much smaller than unity. In other cases it may approach unity (Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1933, Chap. IV), though usually only for reactions involving an ion (Grant and Hinshelwood, J., **1933**, 258). It seemed possible that chemical changes might fall into two well-defined classes of slow and fast, determined by the presence or absence of some special factor, such as a quantum-mechanically forbidden electronic transition ; but experiments have not supported this idea (Hinshelwood and Legard, J., 1935, 587; Hinshelwood, J., 1935, 1111; *Bull. Soc. chim.*, 1935, **2**, 1786). We are inclined now to the opinion that there is no sharp division between the two classes, and, moreover, that the whole of the continuous range of behaviour can, if necessary, be interpreted along more or less classical lines. This conclusion is based upon the statistical survey given in a later section (p. 375). Before discussing these statistics, it is desirable to examine the appropriateness of the representation of reaction velocity in the form $PZe^{-E/RT}$. Other methods of treatment are used, and, in particular, the analysis of the temperature-independent factor of the Arrhenius equation into a collision factor and a steric factor has been criticised. Alternative methods of treatment are therefore first considered, the relation of these to the collision method being in any case a matter of some interest. We shall reach the conclusion that the discussion of the problem in terms of the factor P has an interest of its own, and that we are justified in basing our survey upon it.

The Transition-state Method.—In this method (Eyring, *J. Chem. Physics*, 1935, **3**, 107 ; Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875) the activated molecules are treated as an independent species in equilibrium with the reactants. Statistical mechanics already provides an expression for the absolute value of such an equilibrium constant. The calculation (Fowler, " Statistical Mechanics," Cambridge, **1929**, Chap. 5) is an elaboration of that by which the Maxwell–Boltzmann law is derived. One works out the total number of complexions of the system, taking into account, not only all the ways in which all the atoms and molecules present can be assigned to the different energy levels, but also the number of ways in which the various atoms can be free or distributed among the various molecules present. In doing this, a special hypothesis must be made. The number of molecules in a given quantum state is a perfectly definite number ; the number in a given non-quantised translational state is an indefinite number, depending upon what limits are allowed in defining the state. To introduce a definite correspondence, a range of space and velocity co-ordinates such that $m.du.dx = h$ is taken as the equivalent of a single quantum state. The condition that the number of complexions shall be a maximum gives the equilibrium constant. The expression is of simple form, each concentration term in the chemical equilibrium constant is replaced by the energy-partition function of the corresponding molecular species, and the product is multiplied by $e^{-E/RT}$ where E is the energy absorbed in the reaction. Each partition function is itself a product of separate partition functions for translational, vibrational, and rotational energy. For

a translational degree of freedom, the partition function assumes the form $\sqrt{2\pi mkT}/h$, for a vibrational degree $1/(1 - e^{-h\nu/kT})$, for a two-dimensional rotational motion $8\pi^2IkT/h^2$, and for a three-dimensional rotation $8\pi^2(8\pi^3I_1I_2I_3)^{\frac{1}{2}}(kT)^{\frac{3}{2}}/h^3$, where I is a moment of inertia, m a mass, and ν a vibration frequency. (Statistical weights are omitted.)

If we write the equilibrium constant expressing the concentration of activated mole cules in terms of that of the reactants in the form

$$K = \left(\frac{\text{Product of partition functions for active complex}}{\text{Product of partition functions for reactants}}\right) \times e^{-E/RT}$$

where E is the activation energy, then the rate of reaction may be set proportional to this expression, which is called the probability of the activated state. Without going into the question of the validity of the interesting method by which Eyring seeks to obtain the absolute reaction rate by multiplying such an expression by a thermal translational velocity, it may be said that valuable information can be obtained by considering the relative values of K for different types of case. For example, one may compare K for a reaction involving the union of two complex molecules, with the value K_a for the union of two atoms to form a diatomic molecule (Evans and Polanyi, *loc. cit.*; Bawn, *Trans. Faraday Soc.*, 1935, **31**, 1536). K will contain three translational partition functions, a three-dimensional rotational, and n vibrational partition functions for the active transition complex of the two reactants, divided by six translational, two three-dimensional rotational, and l vibrational partition functions for the two separate reactants. We may represent this symbolically by $T^3R^3V^n/T^6R^6V^l$. Since the total number of degrees of freedom before and after union of the reactant molecules to the complex must be the same, $l = n - 6$. K_a, on the other hand, will contain T^3 and R^2 and V for the diatomic molecule, divided merely by T^6 for the two atoms, giving T^3R^2V/T^6. (We are not formulating one of the vibrations here as a translation along a co-ordinate in which decomposition occurs : this is unnecessary, since the corresponding terms will cancel in the ratio K/K_a.) If the energies of activation are equal for the two kinds of reaction under consideration, K/K_a becomes of the form V^5/R^5, *i.e.*, a product of five one-dimensional vibration functions divided by a three-dimensional and a two-dimensional rotation function. The vibrational functions are those of the new vibrational degrees of freedom which come into being when half the translations and rotations of the reacting molecules lose their individuality in the complex. If $h\nu$ is fairly small, V reduces to the form $kT/h\nu$; R, apart from a small numerical factor, is $\sqrt{2\pi IkT}/h$ (the exact product R^3R^2 is easily worked out). Bawn (*loc. cit.*), taking $kT/h\nu$ as equal to unity for each of the V terms, and all the moments of inertia to be 10^{-39}, shows that V^5/R^5 may be very small. Thus if P were unity for the atomic reaction, it would be very small for the reaction of the complex molecules.

Comparison of the Transition-state Method and the Collision Method.—The question is whether the transition-state method can be regarded as superseding the collision method. It is objected that the collision diameter used in calculating Z is an unsuitable quantity to deal with, because it is the distance at which transfer of momentum occurs, and, although significant in the discussion of transport phenomena, is only arbitrarily related to chemical interaction. This, however, is a matter of taste. In the collision method we consider the two molecules at the distance for momentum transfer (which, incidentally, is fairly well related to crystallographically-determined distances), and inquire what further conditions of orientation and internal state, relative velocities of pairs of atoms, and so on, must be fulfilled. These conditions are evidently difficult to specify. In applying the transition-state method, however, the difficulties are really as great, and the arbitrariness of the assumptions which must be made to obtain a numerical answer is only less apparent. In the problem discussed in the last section, $kT/h\nu$ was taken as unity, while the moment of inertia was so chosen that R was a quantity of the order 10. With these values a very small P followed naturally. But the vibrations concerned are those of newly-formed degrees of freedom in an active molecule where the binding may be very loose : thus $kT/h\nu$ might in fact be much greater than unity, and when five such terms are multiplied together a whole range of different results can be obtained. Again, three of the R terms refer to the active

complex, and the assumption that this has a normal moment of inertia is equivalent to specifying fairly exactly the distance of the molecules at the instant of chemical transformation. To obtain a small value of P we also had to assume that $h\nu/kT$ was not very small compared with unity, the new vibrations in the critical complex being those of not too loosely bound atoms. In other words, each pair of atoms which form a new link must be not too far from their stable positions—not stretched apart, for example, so that the vibrations are near a convergence limit. This, therefore, seems to be equivalent to demanding a rather exact orientation of the colliding molecules as a whole, and probably also a fairly exact definition of the exact phase of their motion which certain atoms are in. To specify the five V terms correctly and obtain the exact value of P is in essence as difficult as to specify the orientations and phases correctly.

It seems, then, that the collision theory is not really at a fundamental disadvantage, if, as a matter of taste, we prefer to approach the problem in that way. The conclusion is that we should seek all the help we can obtain by applying both methods. Though the transition-state method works in terms of quantities which are themselves of a more general significance, assuming that we know them, the specification of the collision conditions must always retain some independent interest.*

Consideration of Entropy Changes.—The entropy change in a chemical reaction is related to the equilibrium constant by the well-known thermodynamic equations $\log K = U/RT + S/R$ (where U is the difference of the activation energies for the two opposing reactions), and $K = k_1/k_2$. Hence $\log k_1 - \log k_2 = S/R - E_1/RT + E_2/RT$. Since $\log k = A - E/RT$, it follows that $A_1 - A_2 = S$. Very interesting relations between S and the separate values A_1 and A_2 may be observed (cf. Soper, J., 1935, 1393; Rice and Gershinowitz, *J. Chem. Physics*, 1934, 2, 853; Rodebush, *ibid.*, 1933, 1, 440), but it does not seem possible in any generally valid way to derive A_1 and A_2 from S. It may be possible to split S into two terms such that $S = f(S_1) - f(S_2)$, where $f(S_1)$ and $f(S_2)$ are respectively functions of reactants only and products only, but these two quantities will not necessarily equal A_1 and A_2; for we might have $A_1 = f(S_1) + C$ and $A_2 = f(S_2) + C$, and C may be as important as any of the other terms. Thus we cannot, without special justification, calculate P from $f(S)$. This was clearly stated by van 't Hoff ("Lectures," English transl., p. 214) in his discussion of the influence of solvents on reaction velocity. He pointed out that the solvent has two effects, one acting on the two opposing reactions to an unequal extent and producing the thermodynamically calculable equilibrium shift, and the other operating equally, to an unknown extent, on the forward and the reverse reaction.

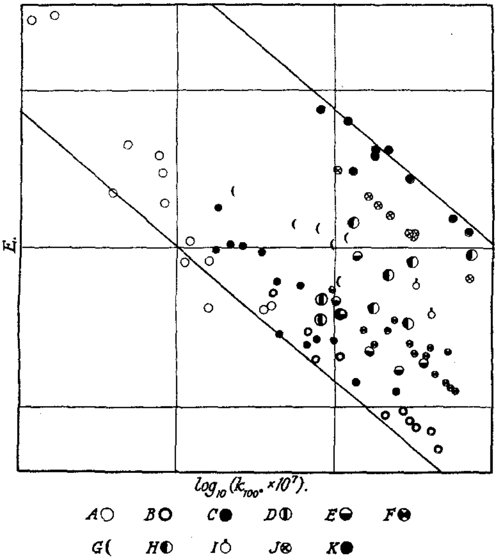
That the limitation of the thermodynamic method is real and not merely formal, is shown by the fact that P may be a function of the catalyst employed, *e.g.*, in esterification

* The present method of approach is not inconsistent with the view that the reactive species is sometimes a definite complex (see, *e.g.*, Conant and Bartlett, *J. Amer. Chem. Soc.*, 1932, **54**, 2881). The concentration of such complexes will vary with temperature, and this introduces a difference between the observed activation energy, obtained from the Arrhenius equation, and the activation energy which the complex itself must possess in order to react. This fact might seem to call for a modification of the ordinary collision treatment, but the difference is really only a formal one. If two reactants, X and Y, form reversibly a complex XY with evolution of heat Q, then the concentration of XY, as long as it is small compared with that of X and Y, is given by van 't Hoff's equation, $[XY] = \text{const.}\ [X][Y]e^{Q/RT}$. If the complex itself requires an activation energy E_c for further change, its rate of reaction will be proportional to $[XY]e^{-E_c/RT}$, and thus the rate expressed in terms of the reactants will be const. $[X][Y]e^{-(E_c - Q)/RT}$. The Arrhenius activation energy will be $E_c - Q$, *i.e.*, less than E_c. This, however, does not explain why the reaction proceeds at a smaller rate than might have been expected from the observed value, $E_c - Q$. For molecules which bring only $E_c - Q$ can form a complex, which, by hypothesis, will now contain $E_c - Q + Q$, and thus possesses the activation energy necessary for further reaction. Why it does not react immediately but persists and is perhaps later resolved into its products once more, is the same problem as before. The same argument applies *mutatis mutandis* to the case of an endothermically formed complex. We have then the state of affairs that molecules which bring the *observed* activation energy into a collision can give a complex possessing the algebraic sum of the observed activation energy and the heat of formation of the complex, *i.e.*, the true activation energy of the complex, yet reaction does not occur except in a fraction of the encounters. This fraction, as before, is P.

reactions (Williamson and Hinshelwood, *Trans. Faraday Soc.*, **1934**, **30**, 1145; Hinshelwood and Legard, J., 1935, 587, 1588), or in the acetone–iodine reaction (Smith, J., **1934**, **1744**). Since the equilibrium constant cannot be altered by the catalyst, P cannot be calculated in these cases from thermodynamic quantities alone. This does not preclude the existence of striking correlations between P and the position of equilibrium in certain types of reaction (compare Evans and Polanyi, *loc. cit.*).

The experimentally observed Values of P *for Bimolecular Reactions in Solution.*—A convenient way of representing experimental results is to plot log k against E for series of related reactions, examples being chosen in each series to cover as wide a range of velocity as possible. In this way it is easy to decide whether relations between k, E, and P are

FIG. 1.



significant and characteristic or merely accidental. Several series have now been studied in this way, and the results are collected together in Fig. 1. The series included are the following:

A. Esterification in alcoholic solution, the catalyst being the undissociated acid molecule (Hinshelwood and Legard, *locc. cit.*).

B. Benzoylation of aniline as modified by nuclear substituents (Williams and Hinshelwood, J., 1934, 1079; Newling, Staveley, and Hinshelwood, *Trans. Faraday Soc.*, **1934**, **30**, 579).

C. Quaternary ammonium salt formation in benzene solution (Winkler and Hinshelwood, J., **1935**, 1147).

D. Two examples only: interaction of acetic anhydride and alcohol in two solvents (*Moelwyn-Hughes and Hinshelwood, J., 1932, 230*).

E. Esterification with hydrion as catalyst (Hinshelwood and Legard, *loc. cit.*).

F. Halogenation of phenolic ethers (Bradfield and Jones, J., 1928, 1006, 3073; 1931, 2903, 2907. Here about half the available points, chosen at random, are plotted).

G. Reaction between trinitroanisole and ring-substituted dimethylanilines (Hertel and Dressel, *Z. physikal. Chem.*, 1935, *B*, 29, 178).

H. Oxidation of cyclic compounds by potassium permanganate (preceding paper).

I. Two examples only: additions to dienes (Wassermann, J., 1935, 828).

J. Alkaline hydrolysis of substituted benzoic esters (Ingold and Nathan, this vol., p. 222. We are indebted to Prof. Ingold for advance communication of these results).

K. Interaction of alkyl halides and negative ions. [Three of the points refer to the results of Grant and Hinshelwood for the reaction of potassium hydroxide with ethyl halides (J., 1933, 258), and the others are the first five values given by Moelwyn-Hughes (*op. cit.*, table, p. 79). They could be supplemented by others from this same table, but the range of E values would not thereby be extended, nor would the degree of departure of the points from a single line be appreciably changed. The values given are justly representative of the whole set.]

Of these, D and I transgress the principle that a whole series should be available, but they are included as examples of interesting types of reaction, meriting further study.

The values of k are all calculated to 100° and expressed in g.-mol./l./sec. The two diagonal lines in Fig. 1 are of the standard slope, $2{\cdot}303RT$, and in positions corresponding to $P = 1$ and $P = 10^{-8}$ respectively.

In any given series the tendency of the points to group themselves about a line of the standard slope is evident, except that in series A there is an increase in the slope towards the higher values of E. Both the position of the mean standard line for any series and the deviations of the individual points from it are of interest. The following simple statistical analysis was therefore made. By the method of least squares the best line of slope $2{\cdot}303RT$ was drawn through the points for a given series, only the two points for the highest E values in series A being omitted. This line cuts the ordinate corresponding to $\log k \times 10^7 = 0$ at a value b. Since $k \times 10^7 = cPZe^{-E/RT}$, where c is a constant for the conversion of units, $2{\cdot}303RT \cdot \log (k \times 10^7) = 2{\cdot}303RT \cdot \log (cPZ) - E$, whence $b = 2{\cdot}303RT \cdot \log (cPZ)$. For series K we know that P is almost exactly unity. The variations of Z from case to case are small and are neglected: hence from the value of b for series K we find c, and hence the absolute values of P for the other series.

To convey an idea of the distribution of the individual values in a series about the mean, the Gauss curves shown in Fig. 2 have been constructed. Although there are not enough examples in any series to establish the exact form of the frequency distribution curve, the assumption of the symmetrical form is unobjectionable in representing the range of the deviations. The constant a in the equation of the curves $y = e^{-a^2x^2}$ is found for each series by measuring the range of log P which includes approximately half the points, and then using a table of error functions and their integrals.

Figs. 1 and 2 both show that there is a fairly continuous transition from the fast to the slow type of reaction. Fig. 2 shows further that there is considerable variation in the degree of conformity to the mean type of behaviour.

Factors influencing P.—We may now attempt to estimate the range over which P might theoretically be expected to vary. For this purpose we tabulate first a series of factors which tend to make P small, and assign a rough but, we think, not unreasonable figure for the ratio in which perfect efficiency of activating collisions might be reduced by the operation of each.

(1) The reactive groups of the colliding molecules must be presented to one another in correct orientation. We might plausibly take 1/10 of each molecular surface as active in an unfavourable case. Thus according as two or three molecules are involved (three, for example, with acid, catalyst, and alcoholic solvent), the inefficiency factor could be anything from unity down to 10^{-2} or 10^{-3}.

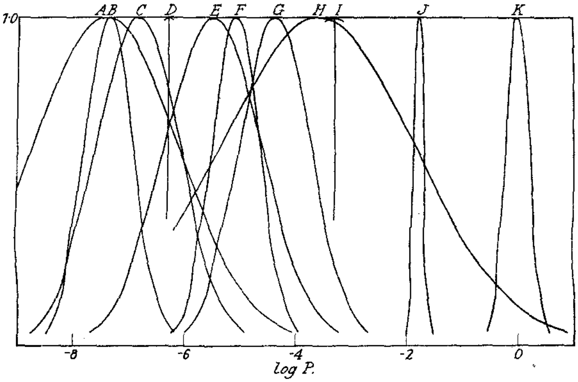
(2) New linkings must be formed and existing ones broken. A link is most easily broken when the two atoms are at the extreme of the amplitude of their vibration. Thus, even when the link is activated, there may be only a comparatively narrow range of phase in

which actual rupture occurs. This might easily correspond to 1/10 only of the whole period. Changes in at least two links are usually involved, so that a factor of 10^{-2} would not be surprising.

(3) Groups may be present in the molecules which impede access to the reactive centres. Although steric hindrance is overcome mainly by increased activation energy, approach to the active centres may still only occur when the hindering groups are in that phase of their bending oscillations which opens the widest angle of access. A factor of 10^{-1} is reasonable here.

(4) In some reactions the solvent must play an intimate part which does not appear in the chemical equation. Several attempts have been made to study typical solution reactions in the gas phase, and the reaction has usually been proved to occur not homogeneously but in an adsorbed film (cf. J., 1932, 230; *Trans. Faraday Soc.*, 1935, **31**, 1739). The continuous medium round the reacting molecules is thus in some way highly important. Moreover, the value of P varies over a considerable range from solvent to solvent. Thus

FIG. 2.



the orientation of the solvent molecules round the activated complex can be of great importance. For example, in a reaction such as quaternary ammonium salt formation the solvent dipoles might need to be orientated in such a way as to produce a field capable of stabilising the polar form of the transition complex. The probability of the correct orientation is very difficult to estimate, but as a rough approximation we may take each active complex to be surrounded by an octahedral distribution of solvent molecules, each one of the six having a "right" and a "wrong" orientation. The chance that all are right is 1/64, from which we will only conclude that a factor of the order 10^{-2} is possible.

If all these adverse factors combine, P will be of the order 10^{-8}. Their influence, however, may be modified by the following :

(I) Smallness or simplicity of the reacting molecules reduces the effect of all four factors.

(II) Anything which lengthens the duration of collisions will modify (2), (3), and (4). As a special case of a lengthened collision time we may have definite complex formation.

(III) Ionic charges on the reactants may remove the effect of (1) by producing automatically a favourable orientation. They may also affect (4) and enhance (II).

(IV) If, as is possible in certain catalytic gas reactions (cf. J., 1935, 1111), specific kinds

of energy transfer occur in the activating collisions, the molecules may behave as virtually simpler structures than they really are, with consequent increase of P.

In the most favourable case these factors may raise P to unity. The balance between them and the adverse factors (1)—(4) may be expected to give any value between unity and 10^{-8}. To decide how the balance is made up in a given reaction is a matter of no small difficulty, but hardly greater than that of assigning the correct values to all the quantities used in the statistical-mechanical treatment. In a general way it may be said that in series K ($P = 1$) factors (I) and (III) are apparently of decisive importance, that factor (III) accounts for the marked difference between A and E, and that in the reactions where polar salts are formed factor (4) is evidently very important. On the whole, it may be said that the results are quite understandable even though they would have been hard to predict in detail. The range of divergence from the averages can also be understood in a general way. When the reactive group is highly localised, or the group modifying the rate is remote from the active group, the departures from the mean will be small. The benzoylation reaction is a good example of this, as also is series J. In the esterification series, the reacting groups are much more closely incorporated in the main structure and the range of variation is correspondingly wider. The same applies with greater force to the ring-breaking oxidation reactions where the structural factor must be as great as to give rise to what is virtually a change in mechanism from case to case. Within the total range of variation of P in a given series, various regularities, such as correlations between E and P, and so on, are possible (J., 1935, 1111; cf. Evans, Morgan, and Watson, *ibid.*, p. 1167).

If second-order gas reactions are regarded from this point of view, factor (I) would seem to be the governing one, though in some catalytic reactions (IV) may play an important part.

First-order reactions, in gases and in solution, present a rather different picture. When only one molecule reacts, the process does not have to be completed in the short time of a collision, and the preactivated molecule may draw upon the energy stored in any of its parts. If the molecule is complex, this may give rise to a rate of reaction far greater than $Ze^{-E/RT}$. In this sense P becomes much greater than unity. Examples are well known for both gases and solutions. The range over which P may vary is from about unity to 10^5. Thus, taking both first- and second-order reactions into account, we have a continuous range of P values from 10^{-8} to 10^5. In a general way we are now in a position to say where approximately, though by no means quantitatively, a reaction of a given type will occur in this spectrum of P values. Though the full interpretation may possibly involve factors as yet unknown, and quantum-mechanical explanations may be necessary for some of the more detailed relations (compare Bell, *Proc. Roy. Soc.*, 1936, in the press), relatively simple ideas can give at least a qualitatively satisfactory explanation of the whole range of observed behaviour.

SUMMARY.

The transition-state method and the collision method of treating bimolecular reactions are compared, and it is concluded that the latter method is quite appropriate for a general discussion of the problem. A statistical survey of bimolecular reactions in solution is made in terms of the collision theory.

The factors influencing the value of P in the equation, rate $= PZe^{-E/RT}$, are discussed, and the conclusion is reached that the whole range of observed behaviour can, if necessary, be understood, qualitatively at least, in terms of relatively simple classical ideas.

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90. *The Reaction of Nitric Oxide with Hydrogen and with Deuterium.*

By C. N. HINSHELWOOD and J. W. MITCHELL.

AN earlier investigation (Hinshelwood and Green, J., 1926, 730) of the interaction of nitric oxide and hydrogen led to the conclusion that the principal reaction was homogeneous and termolecular, the rate at pressures greater than a few hundred mm. being proportional to $[NO]^2$ and to $[H_2]$. The curve of rate against hydrogen pressure was linear, but when produced did not pass through the origin, a fact which was explained by the assumption of a heterogeneous reaction independent of the hydrogen pressure, and addition of silica powder to the reaction vessel showed the existence of some surface reaction at the lower pressures. The problem has now been reinvestigated with the objects, first, of making a more detailed examination of the influence of the surface in view of the possibility of long reaction chains, as in certain other oxidation reactions, and secondly, of comparing the reaction of hydrogen with that of deuterium.

The study of the surface effect has given no evidence of the existence of chains. It has shown, however, that the original crude method of varying the surface by adding powdered silica gave an exaggerated idea of the proportion of heterogeneous reaction. The intercept made by the curves of rate against hydrogen pressure now proves to be unchanged by considerable variations of surface. Thus the complex behaviour at low pressures is part of the homogeneous reaction mechanism, which must now be reconsidered.

Measurements have been extended to lower pressures, and it is found that between 50 and 100 mm. the curve of rate against hydrogen pressure for constant [NO], instead of continuing linearly to a finite intercept, bends round and passes through the origin. We have thus to account for the following terms in the equation expressing the reaction rate: a term linearly proportional to $[H_2]$, one increasing initially with $[H_2]$ but reaching a constant limit at comparatively low pressures, and a term proportional to $[NO]^2$ at higher pressnres, but including one proportional to [NO] at lower pressures. These results can be explained by the hypothesis that the reaction is essentially termolecular, but involves binary collision complexes of different lives.

Theoretical Considerations.—The shape of the lower part of the hydrogen-dependence curve is reminiscent of the behaviour of unimolecular reactions in the region where the constant falls off, and suggests the following analogy. If two molecules of nitric oxide collide and remain united long enough to be almost certain of meeting a suitably activated hydrogen molecule, the reaction rate will be independent of $[H_2]$. If, however, the hydrogen pressure is low enough, the average time elapsing before reaction will be greater than the life of the complex, and the rate will be proportional to $[H_2]$. Let [X] be the concentration of the binary collision complex. The latter is formed at a rate $c_1[NO]^2$, and dissociates spontaneously at a rate $c_2[X]$: it reacts with hydrogen at a rate $c_3[X][H_2]$. In the steady state $c_1[NO]^2 - c_2[X] - c_3[X][H_2] = 0$, whence the rate of reaction $c_3[X][H_2]$ is equal to $c_3c_1[NO]^2[H_2]/(c_2 + c_3[H_2])$, which may be written $k[NO]^2[H_2]/\{1 + b[H_2]\}$. This expression varies with $[H_2]$ in the way required.

If a binary collision complex of two nitric oxide molecules is concerned in the reaction, there is, in principle, no reason why a collision complex NO,H_2 should not also play its part, reacting with nitric oxide. The corresponding term in the rate equation will be $k[NO]^2[H_2]/\{1 + b[NO]\}$. We must take into account the limiting case of almost simultaneous ternary encounters, which adds the term $[NO]^2[H_2]$. The complete equation for the reaction rate now becomes

$$k_1[NO]^2[H_2] + \frac{k_2[NO]^2[H_2]}{1 + a[NO]} + \frac{k_3[NO]^2[H_2]}{1 + b[H_2]}$$

This will itself be only an approximation, since a whole range of lives may be expected for each type of complex, just as in the more elaborate theories of unimolecular reaction rate. Even with the form given, it is hopeless to disentangle the constants from the integrated form. Consequently, the initial rates have been measured as carefully as possible over a

wide range, by drawing tangents to large-scale reaction–time curves. As well as can be expected, the results at 801° are summarised by the following formulæ :

For hydrogen, rate (mm./100 secs.) $= 1\cdot0[NO]^2[H_2] + \dfrac{30[NO]^2[H_2]}{1 + 8\cdot0[NO]} + \dfrac{11[NO]^2[H_2]}{1 + 3\cdot4[H_2]}$

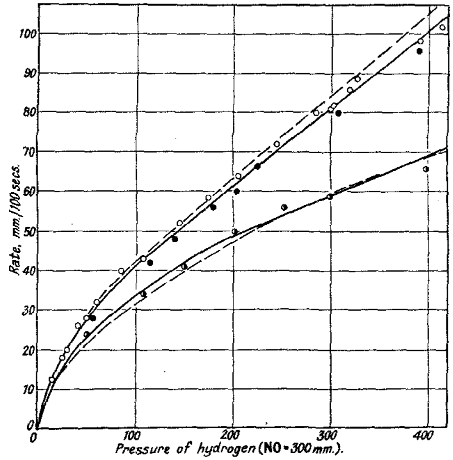
and for deuterium, rate $= 0\cdot7[NO]^2[D_2] + \dfrac{12\cdot5[NO]^2[D_2]}{1 + 8\cdot0[NO]} + \dfrac{7\cdot7[NO]^2[D_2]}{1 + 2\cdot4[D_2]}$

The concentration unit is 100 mm. at 801°.

Experimental.

Apparatus of the type used has been previously described : it consisted of a fused silica reaction bulb, heated in an electric furnace, and connected by capillary tubing to a manometer,

Fig. 1.



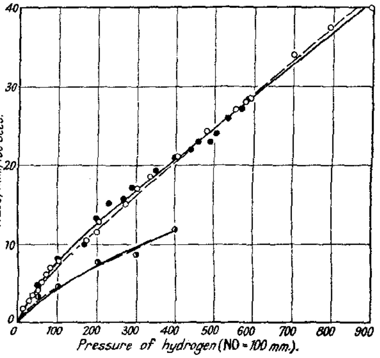
In all the figures the continuous lines represent the experimental results and the broken lines the values calculated from the formulæ. The open and the shaded circles refer to experiments with hydrogen in the unpacked bulb and tube-packed bulb respectively, the half-shaded circles to experiments with deuterium.

to a pre-mixer, and to reservoirs of nitric oxide and hydrogen or deuterium. The capillary tubing was heated to 100° to prevent condensation of water. Electrolytic hydrogen was freed from traces of oxygen by passage over a hot tungsten filament and was dried with phosphoric oxide. Nitric oxide was prepared by the nitrometer reaction. In all the low-pressure measurements the gases were mixed outside the reaction bulb, but at higher pressures experiments with gases mixed within or without the bulb gave identical results. The temperature was measured by a platinum–platinum-rhodium thermocouple. The present results are uniformly about 30% faster than those of the earlier experiments. Since the reaction is quite reproducible, the difference is to be ascribed to a temperature error, which is understandable since, in the original series, a base-metal thermocouple had to be used and its calibration had caused difficulty. In the present series two couples and two indicators were used, and gave concordant results.

Influence of the Concentrations of the Reacting Gases.—All initial rates are expressed as *pressure change (in mm.) per 100 seconds*. The curves showing the variation of the initial rate with hydrogen pressure for constant nitric oxide pressures of 300 and 100 mm. respectively are given in

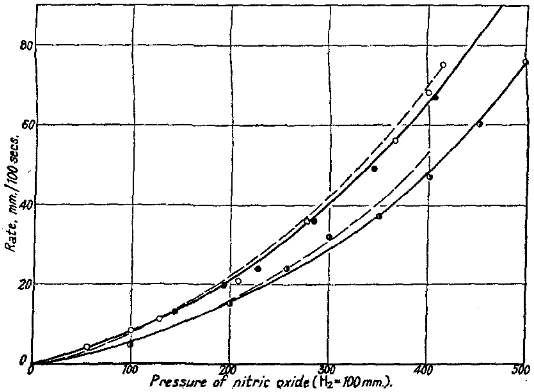
Figs. 1 and 2, and the corresponding data in Tables I and II. The variation of rate with nitric oxide pressure for constant hydrogen pressures of 100 and 300 mm. respectively is represented in Figs. 3 and 4, and the results collected in Tables III and IV.

FIG. 2.



Influence of Surface on the Rate of Reaction.—In order to vary the surface and free space, three reaction vessels were used: an unpacked silica bulb of about 300-c.c. volume, a similar bulb packed with lengths of silica tubing, and a somewhat smaller bulb entirely filled with small, spherical, silica beads. In the last two bulbs the *initial* rates were the same as for the unpacked bulb, but the total pressure changes in 100 seconds were respectively 3% and 6% less. The effect can be explained by consideration of the ratio of the dead space to the reaction space in the different bulbs. The reaction rate depends upon a high power of the pressure, so that quite a small increase in the dead space produces an apparent diminution of the reaction rate. The experiments with the packed bulbs, therefore, point to the non-existence of long chains. But the possibility of an accidental balancing of increased heterogeneous reaction by decreased chain reaction remained. This is in the highest degree improbable for two reasons. If such a balancing occurred in one of the packed bulbs, it would not occur in the other, where the

FIG. 3.



ratio of increased surface to diminished chain length would be quite different. Furthermore, the balancing of two such different effects could not leave the shapes of the complex curves in Figs. 1—4 unchanged, as they are in fact found to be. Since iodine is known to break the chains in the hydrogen–oxygen reaction, a further test for chains was made by the addition to

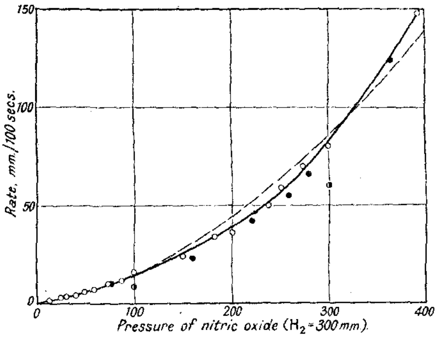
the reaction system of 0·2 mm. of *iso*propyl iodide, which decomposes to give an iodine concentration of about 0·04 mm. The initial rate was increased, and under no conditions could an inhibition be observed. This suggests the absence of a chain mechanism involving atomic hydrogen.

Discussion.

An equation has already been deduced which might be expected to account for the experimental results. It is now necessary to test this and to determine the constants. The constants k_3 and b can be determined separately from the low-pressure part of the curve for variable hydrogen pressures as follows. The terms in k_1 and k_2 contribute to the rate an increment, proportional to the hydrogen pressure, which can be found by producing the linear part of the curves in Figs. 1 and 2 to meet the axis, and then subtracting the intercept. From the total rate, R, we subtract the contribution r from the linear terms; $R - r$ thus represents the contribution to the rate of the term $k_3[NO]^2[H_2]/(1 + b[H_2])$, or $1/(R - r) = 1/(k_3[NO]^2[H_2]) + b/(k_3[NO]^2)$.

For the curve for 300 mm. of nitric oxide, the concentration unit of 100 mm. being used, $1/(R - r) = 1/(9k_3[H_2]) + b/(9k_3)$. If this equation is applicable, $1/(R - r)$ plotted against $1/[H_2]$ should give a straight line of slope $1/9k_3$ making an intercept on the axis of $b/9k_3$. This was confirmed, and from the curve, k_3 was found to be 11·0 and b to be 3·4. The remaining constants were determined largely by trial and error, being finally adjusted so as to make the mean differences between calculated and observed values as small as possible for all four curves. The calculated values are given in Tables I—IV and are also shown by curves in the corresponding figures. No adjustment of the other constants allows the term reducing to a linear function of [NO] to be dispensed with.

Fig. 4.



The Reaction with Deuterium.—Deuterium was prepared by the decomposition of 99·2% deuterium oxide (*d* 1·1079) by passage over activated iron at 560°. Control experiments with hydrogen were made at intervals and gave results concordant with those previously obtained. The results with deuterium are shown in Table V. The investigation was not made in great detail, it being assumed that the rate would follow an equation of the same form as that established for hydrogen. A set of constants was found which would reproduce the experimental curves within the limitations imposed by the use of initial rates.

The constants for deuterium bear to those for hydrogen a ratio of 0·7 : 1·0 in those terms which are concerned with collisions between nitric oxide and hydrogen or deuterium. Most of the difference can be accounted for by the different molecular speeds. The second term of the expression for the rate needs further consideration. If [X] is the concentration of the binary collision complex NO,H_2 or NO,D_2, then in the steady state

$$\gamma_1[NO]\{[D_2] \text{ or } [H_2]\} - \gamma_2[X] - \gamma_3[X][NO] = 0$$

and the reaction rate is

$$\gamma_3[NO][X] = \frac{\gamma_3\gamma_1[NO]^2\{[H_2] \text{ or } [D_2]\}/\gamma_2}{1 + \gamma_3[NO]/\gamma_2}$$

TABLE I.

Unpacked bulb; 801°. Constant initial press. of NO = 100 mm. | Packed bulb; 801°. NO = 100 mm.

H_2, mm.	Rate. Obs.	Rate. Calc.	H_2, mm.	Rate. Obs.	Rate. Calc.	H_2, mm.	Rate.	H_2, mm.	Rate.
13	1·8	—	(300)	16·6	15·9	48·5	4·8	438	22
27·8	2·8	—	304	17	—	101	7·9	457	23
35	3·5	—	335	18·5	—	166	10·0	487	23
(50)	4·8	4·2	(400)	20·8	20·3	200	13·2	504	24
60	5·2	—	401	21	—	230	15·2	532	26
70	6·2	—	478	24·4	—	266	15·6	568	27·2
80	7·0	—	533·5	27	—	290	17·2	585	28·4
(100)	8·0	6·8	578	28	—	350	19·4		
100	8·2	—	591	28·5	—	397	21		
173	10·5	—	(600)	29·2	29·1				
(200)	12·5	11·5	700	34	33·6				
204·5	12·8	—	794	37·5	—				
273	15	—	896	40	42·0				

Results in parenthesis are taken from the smoothed curve.

TABLE II.

Unpacked bulb; 801°. Constant initial press. of NO = 300 mm.

H_2, mm.	Rate. Obs.	Rate. Calc.	H_2, mm.	Rate. Obs.	Rate. Calc.	H_2, mm.	Rate. Obs.	Rate. Calc.	H_2, mm.	Rate. Obs.	Rate. Calc.
15	12·5	—	60	32	—	(200)	62	65·0	303	82	—
25	18·0	—	85	40	—	206	64	—	319	86	—
30	20·0	—	(100)	42	42·4	246	72	—	327	88	—
41	26·0	—	108	43	—	285	80	—	391	98·5	—
(50)	29·0	28·3	145	52	—	(300)	82	85·9	(400)	102	106·3
50	28	—	175	58·5	—	300	81	—	414	102	—

The results for the packed bulb are similar. They are shown in the figure but not tabulated in detail.

TABLE III.

Unpacked bulb. Constant initial press. of H_2 = 100 mm.

NO, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	Rate. Obs.	Rate. Calc.
56	4·4	—	(200)	20·6	21·1	(300)	40	42·4	(400)	68	70·5
(100)	8·4	6·8	208	21	—	300	42	—	400	68	—
129	11·2	—	279	36	—	365	56	—	416	75	—

The experiments in the packed bulbs are shown in the figure, the data not being tabulated.

TABLE IV.

Unpacked bulb. Constant initial press. of H_2 = 300 mm.

NO, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	Rate. Obs.	Rate. Calc.
12	1·5	—	59	7·2	—	150	24	—	250	59	—
24	3·0	—	73	10	—	182	34	—	273	70	—
30	3·4	—	87	11·6	—	200	36	—	300	81	85·9
40	4·0	—	(100)	14	15·9	(200)	38	44·9	393	148	—
49	6·0	—	100	16·6	—	237	50	—	(400)	153	140

Packed bulb. Hydrogen = 300 mm.

NO, mm.	76·5	161	220	258	279	364
Rate	10	22·4	42	55	66	124

γ_1 will depend upon the molecular velocity of deuterium or hydrogen, but γ_3 will not. The activation energies of NO,H_2 and NO,D_2, depending upon different zero-point energies, may well be different. But the influence of the zero-point energy on γ_2 and γ_3 might easily be nearly the same, so that the ratio γ_3/γ_2 remains constant, as appears in the formula

TABLE V.

Unpacked bulb; 801°.

NO, mm.	D_2, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	D_2, mm.	Rate. Obs.	Rate. Calc.	NO, mm.	D_2, mm.	Rate. Obs.	Rate. Calc.
100	50	3·4	—	300	50	24	21·2	200	100	15	14·8
100	(50)	3·4	2·8	300	108	34	—	257	100	24	—
100	100	4·6	4·4	300	(100)	33	31·2	350	100	37	—
100	200	7·6	6·9	300	150	41	—	400	100	47	54
100	300	8·6	—	300	(200)	47	45·6	450	100	60	—
100	(300)	9·1	9·1	300	202	50	—	500	100	76	81·7
100	400	11·8	—	300	253	56	—				
100	(400)	11·3	11·3	300	(300)	60	57·8				
				300	304	60	—				
				300	398	66	—				
				300	400	72	69·5				

used to represent the experimental results. γ_1 being affected both by speed and by zero-point energy, k_3 may differ considerably for the two isotopes, as is in fact found. A more detailed discussion of the various ratios observed would be too speculative to be profitable.

The Influence of Temperature.—The temperature coefficient of the rate was determined for 400 mm. of nitric oxide and 200 mm. of hydrogen, the results being shown in Table VI. In principle, it should be possible to measure the temperature coefficients of all the constants in the equation, but as these constants themselves could not individually be fixed to within less than about 10%, the detailed analysis was considered impracticable. The activation energy found is a complex quantity, but it would be well-nigh impossible to separate the individual values. The Arrhenius equation is obeyed, and gives $E = 47{,}000$ cals. This is a better value than the older one of 44,000, which was probably rendered inaccurate by an undetected drift in the base-metal thermocouple. The three types of process into which we now analyse the reaction differ only in their time relations, and all involve a direct interaction of two molecules of nitric oxide and one of hydrogen. Thus it is quite possible that the various activation energies are all nearly the same: 47,000 cals. will then be nearly the true value. It is quite evident, in any case, that the reaction of nitric oxide and hydrogen has an activation energy of a different order of magnitude from that of the reaction of nitric oxide and oxygen. The qualitative remarks at the end of the earlier paper hold good.

TABLE VI.

Temp.	700°	725°	740°	750°	760°	775°	800°	825°
k	46	84	122	158	193	271	467	776

The velocity constants are calculated from the time of half change by means of the simplified formula

$$k = \frac{1}{t_{\frac{1}{2}}}\left\{\frac{1}{(a-b)^2}\log\left(\frac{2a-b}{a}\right) + \frac{1}{(b-a)}\cdot\frac{b}{a(2a-b)}\right\}$$

where a is the initial concentration of nitric oxide and b that of hydrogen, *i.e.*, that for a third-order reaction. This is nearly true at the pressures used, *viz.*, 400 mm. of nitric oxide and 200 mm. of hydrogen.

The constants are expressed in g.-mol./l./sec.

SUMMARY.

The reaction between nitric oxide and hydrogen has been reinvestigated. No evidence of long reaction chains has been found. The proportion of surface reaction is much smaller than was previously assumed, and the complex behaviour at lower pressures has now proved to depend upon the homogeneous reaction mechanism.

The results can be explained by the hypothesis that the reaction, though essentially termolecular, involves binary collision complexes of different lives.

On this basis an equation was obtained to describe the curves obtained for initial rates with various pressures of nitric oxide and hydrogen.

The reaction of nitric oxide and deuterium at 801° is represented by an analogous equation with different constants.

The temperature coefficient of the reaction with hydrogen has been redetermined.

We are indebted to Imperial Chemical Industries, Ltd., for a grant.

PHYSICAL CHEMISTRY LABORATORY, BALLIOL COLLEGE AND TRINITY COLLEGE, OXFORD.
[*Received, February 5th, 1936*].

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91. *The Concentration of Artificially Produced Radio-elements by Means of an Electric Field.*

By J. W. J. FAY and F. A. PANETH.

ALL methods of producing artificial radio-elements have the disadvantage that only a very small fraction of the atoms exposed to the bombarding particles becomes activated. The radio-elements, therefore, are invariably diluted by an overwhelming mass of inactive material, and for their theoretical study as well as their practical use as indicators it is frequently necessary to extract and concentrate them. Methods for doing this with invisible quantities of active materials have been developed in the study of the natural radio-elements. One of the most efficient is the application of an electric field to either the gaseous or the liquid phase; well-known examples, in the former case, are the collection of the " active deposits " produced by the three emanations; in the latter case, the electrolytic deposition of these and other isotopes of lead, bismuth, and polonium.

It seemed worth while to investigate whether an electric field might also be of help in concentrating artificial radio-elements. We have applied this method in both the gaseous and the liquid phase. As the only available neutron source was small, experiments had to be confined to the study of artificial radio-elements produced by slow neutrons, since only this type of activation can be increased by the " hydrogen effect "; whence it follows, further, that in our experiments the artificial radio-elements were necessarily isotopes of the bombarded ones. It should be pointed out, however, that the application of an electric field to the concentration of artificial radio-elements is a general method and can certainly be used with advantage, and frequently even in a still more efficient way, in the case of non-isotopic radio-elements produced by neutron bombardment, and of radio-elements generated by the impact of α-particles or protons.

EXPERIMENTAL.

The source of neutrons for producing the artificial radio-elements consisted of 25 mc. of radio-thorium, mixed with 5 g. of finely powdered beryllium and sealed in a glass tube. The neutrons were " slowed down " by performing the experiments in a large tank of water, 40 cm. in diameter and 30 cm. high.

The activity was measured in the usual way, by counting the β-rays by means of a Geiger–Müller counter, the impulses being amplified by a single-stage amplifier and then fed into the grid circuit of a Thyratron valve, which worked a telephone meter, so that each electron entering the counter was automatically recorded.

(a) *Experiments in the Gaseous Phase.**—The gas employed for these experiments was arsine, because arsenic, as Amaldi, d'Agostino, Fermi, Pontecorvo, Rasetti, and Segré (*Proc. Roy. Soc.*, 1935, **149**, 522) have shown, when irradiated with neutrons, gives an isotope according to the equation $^{75}_{33}As + ^{1}_{0}n \longrightarrow ^{76}_{33}As$, and consequently the activation is increased by surrounding it with water; moreover, the half-life period is of convenient length (26 hours), and the activity is strong. Arsine is one of the few gaseous compounds which satisfy these conditions.

The arsine, prepared by reducing an acid solution of arsenious oxide by means of zinc, was purified by passage over soda–lime and calcium chloride and then frozen out in a liquid-air trap. It was stored in an 8-litre bulb, shielded from light. The spontaneous decomposition, on the

* A summary of this part of the paper appeared in *Nature*, 1935, **135**, 820.

walls of the vessel, of gas so purified was almost completely suppressed during storage, and in the actual experiments further precautions (see below) were taken.

The experiments were carried out in a silver flask, of 800-c.c. capacity, fitted with a ground-glass stopper having a side-tube and tap; into the top of the stopper a piece of glass tubing was sealed, reaching nearly to the centre of the flask, and containing a copper lead dipping into mercury and so making contact with the inner electrode, which normally consisted of 10 cm. of platinum wire bent into the shape of a flat, compact zig-zag of length about 1·5 cm. and sealed into the central tube. A minimum of grease was used for the ground-glass joint, since grease catalyses the spontaneous decomposition of arsine. The outer electrode was the flask itself.

Arsine was introduced to the required pressure into the evacuated flask *via* the side tube as follows. The gas was condensed out of the storage bulb in a liquid-air trap and, after any hydrogen resulting from its decomposition had been pumped off, it was passed through a cotton-wool plug into the flask, by removing the liquid air and allowing the trap gradually to warm sufficiently for the gas to distil off. The tap on the side tube was then closed. The cotton-wool filter retained any solid arsenic particles, which catalyse decomposition. Rubber connexions were also eliminated for the same reason.

The flask was then placed in the water-bath, with the source, contained in a boiling-tube, clamped beside it. The flask and the source were so arranged as to be as near as possible to the centre of the bath. All experiments were performed with the same relative distribution.

The field was 1300 volts (about 250 volts/cm.), applied from dry batteries, with a water resistance in each lead as a safety precaution. (Experiments were performed without these resistances in the leads and, as expected, they caused no modification in the results.) The glass stopper was shielded from light during the experiments.

Irradiation was first carried out with the electrodes joined together, and no activity whatever was found on the platinum wire. The field was then applied during irradiation, each experiment being performed with the inner electrode charged negatively and positively alternately. An activity could be collected on the electrode, independently of the sign of the charge. As a check in the first few experiments, the decay curve of the activity was taken, and found to have a half-value period of about 1 day, as was to be expected for the arsenic isotope ${}^{76}_{33}$As. Very occasionally an experiment with the positive charge on the inner electrode during irradiation gave no activity on the electrode; this happened so rarely, however, that we could not study the reason for this failure. The exception did not occur when the inner electrode was negative.

Experimental conditions were varied in different ways; the pressure of the gas and the metal of the electrode were altered; hydrogen and water vapour were added; and the ionisation inside the flask was increased by means of the extra γ-radiation from a 30-mc. radio-thorium source, unmixed with beryllium, placed inside the flask. In some cases these variations caused a deposit of arsenic on the wire about 10^{-4} cm. thick without, in general, increasing the yield of active isotope to any great extent. Hydrogen alone made the collection of the activity completely reliable on either electrode, a fact which may be due to the production of a well-defined platinum–hydrogen surface. In this connexion the effect of cooling the platinum wire in a stream of hydrogen after ignition in a Bunsen flame was tested, but no difference was observed. A few experiments were done with the platinum electrode coated with arsenic, but the yield was appreciably lowered. For all other experiments the platinum wire was carefully ignited.

In order to determine the yield, it is necessary to know the total activity induced in the arsine; for this purpose a small quantity (0·2 g.) of arsenious oxide was irradiated inside the flask under conditions similar to those obtaining during the irradiation of the arsine, and the activity measured directly. As a check, a similar quantity was irradiated inside the flask in solution and precipitated as magnesium ammonium arsenate, after oxidation with nitric acid. The two values agreed within 5%. It was found, as expected, that the yield was proportional to the pressure of arsine in the flask, and for comparison, all results were corrected for 100% activation (*i.e.*, irradiation at a pressure of 76 cm. for 10 days).

In no case was more than 30% of the active isotope collected on the inner electrode, and these higher yields were always accompanied by the deposition of a weighable quantity of inactive arsenic. On the other hand, by very careful purification, up to 15% of the active isotope could be collected on a straight platinum wire of length 3 cm., charged positively or negatively, without the deposition of a visible layer of arsenic. In these experiments, the concentration factor [*i.e.*, the change in the ratio (^{76}As, %)/(^{75}As, %) on the electrode] was certainly greater than 20,000.

A few experiments were performed with a smaller voltage between the electrodes, with the object of finding whether a larger flask could be employed with the available H.T. supply.

A potential of only 250 volts, or 50 volts/cm., was found to be only slightly less effective than the 1300 volts normally employed. Consequently, a copper flask, similar to but larger than the silver flask, was used for a further series of experiments, but the yield did not increase in proportion to the volume.

The results are summarised in Table I.

TABLE I.

Silver flask; diam. 5 *cm., vol.* 800 *c.c.*

Electrode.	Field.	Kicks/ min.	% Activity deposited.	Wt. of As deposited, g.	Concn. factor.
Before shielding gas from light, etc.; gas at about 70 cm.					
Cu plate	−	15	24	—	—
Cu spiral	−	17	26	0·0015	500
,,	+	22	34	0·0036	300
Conditions modified as described on p. 385; gas at about 70 cm.					
Pt spiral	−	16	25	0·0004	2,000
,,	+	12	19	0·0002	2,900
Effect of addition of water (a few drops in bottom of flask); gas at 70 cm.					
Pt spiral	−	6	9	0·0004	600
,,	+	15	24	0·0003	2,400
Effect of reducing pressure: gas at 35 cm.					
Pt spiral	−	14	22	0·000035 *	19,000
,,	+	12	19	0·000035	16,000
Effect of additional radiation: 30-mc. radio-thorium in flask.					
Pt spiral	−	10	16	0·0001	5,000
,,	+	11	17	0·0001	5,000
Effect of addition of hydrogen: 35 cm. AsH_3 + 35 cm. H_2.					
Pt spiral	−	10	16	0·0001	5,000
,,	+	11	17	0·0002	2,500
Effect of using Pt spiral coated with As; gas at 70 cm.					
Pt spiral with some As already on spiral	−	4	8	0·0001 (extra)	
,, ,, ,, ,, ,,	+	2½	4	No weighable extra quantity deposited	

* Thanks are due to Miss P. M. Sanderson for weighing these very small deposits on the microbalance.

Variation of field: 35 *cm.* AsH_3 + 35 *cm.* H_2. Pt *spiral electrode.*

Field	−1300	+1300	−500	+500	−250	+250
Kicks/min.	10	11	8	9	7	6
% Activity	16	17	12	14	11	10

Copper flask; diam. 9 *cm., vol.* 3200 *c.c.* Pt *spiral electrode.*

Field	−1300	+1300	−1300 (with H_2)	+1300 (with H_2)
Kicks/min.	13	7	11	18
% Activity	5	3	4	7

It appears from the results that the active arsenic isotope does not retain any characteristic charge which may possibly be imparted to it at the moment of its formation. It seems probable that clusters are formed, which acquire a charge by catching the ions present in the gas. These ions apparently may be produced by the neutrons as well as the γ-rays (Hopwood and Philipps, *Nature*, **1935**, **136**, 1026); as insufficient is known about the relative intensities of both ionisations, our failure to detect any influence by a rather weak γ-ray source is not surprising.

In convenience and general reliability, the results obtained in the gaseous phase are not to be compared with those obtained with liquids.

(b) *Experiments in the Liquid Phase.*—In these experiments the general arrangements of source, sample, and bath as described above were employed. 10 C.c. of the liquid were irradiated in a boiling-tube fitted with electrodes 1 cm. square; the field (360 volts) was obtained from dry batteries, and except where otherwise stated, it was applied during the whole of the irradiation and removed one minute after the source had been taken away.

It was decided to use organic liquids containing bromine and iodine, inasmuch as these elements are both strongly activated in water with an induced activity of half-life 18 and 25 minutes, respectively (Fermi *et al.*, *loc. cit.*), a very convenient period since 30 minutes' irradiation gives over 50% of the maximum activity, and in all experiments this was the period of exposure. In this time no appreciable activation of the bromine isotope of 4-hours' period occurs.

To find the order of the activity to be expected, similar samples were irradiated under the same conditions but without electrodes, and the active isotope was precipitated by the method of Szilard and Chalmers (*Nature*, 1934, **134**, 462). This gave an activity (corrected for incomplete activation and decay) of the order of 100 kicks/minute, and in making comparisons these values are arbitrarily called 100% for each respective sample. Experiments were made on the activity of irradiated ethyl iodide (liquid) before and after precipitation, and only about 60% of the total activity was precipitated by this method.

Experiments with ethyl iodide, using platinum electrodes, gave no activity on either anode or cathode. Silver electrodes, however, resulted in the collection of the activity exclusively on the anode, the yield being slightly higher than that obtained by the precipitation method (*i.e.*, > 100%). Copper electrodes cleaned with emery gave on each electrode a visible deposit of cuprous iodide with some activity, but the condition of the surface of the electrodes had a great influence, and, by carefully polishing each electrode with fine abrasive powder, it was found that the activity was here also confined to the anode, the yield being somewhat under 100%. If the experiment was performed in exactly the same way, except that no field was put on the electrodes, a low yield of active isotope was collected on the rough copper electrodes, showing that there is a definite affinity of the iodine for the copper, irrespective of the electric field, which can, however, be overcome by application of the field and use of smooth electrodes. It would appear that the chemical affinity is necessary to retain the halogen when it reaches the electrode, and this probably explains the absence of activity on the platinum electrodes.

In order to ascertain whether the negative charge, which the ions must have in order to be collected exclusively on the anode, is a lasting property or merely momentary, the experiment was repeated with no applied field during actual irradiation, the field being applied for 30 minutes after irradiation had been stopped. The yield, after allowance for decay, was practically the same as that previously obtained, being, if anything, a little higher, showing that the charge is retained.

These results, summarised in Table II (i), were obtained by using a fresh sample of ethyl iodide for each experiment, but when the same sample was nsed more than once, after a few hours had been allowed for the old activity to decay, the collected activity was still confined to the anode but the yield decreased continuously until finally practically no activity was collected; this suggests that an exchange of electric charges between the radio-active iodine and a small quantity of iodine ions present in the liquid takes place. This point was investigated subsequently (see p. 388).

A similar series of experiments was carried out, with bromoform instead of ethyl iodide. The results are in Table II (ii).

TABLE II.

			(i) *Ethyl iodide.*				(ii) *Bromoform.*			
			Anode.		Cathode.		Anode.		Cathode.	
Electrodes.	Treatment.	Field.	Kicks/ min.	%.†	Kicks/ min.	%.†	Kicks/ min.	%.†	Kicks/ min.	%.†
Pt	Ignited	360	0	0	0	0	0	0	0	0
Ag	Abrasive powder	360	145	120	0	0	10	6	10	6
Cu	Emery	—	13	11	13	11	21	13	22	13
"	"	360	90	75	20	17	17	11	17	11
"	Abrasive powder	360	100	84	0	0	23	15	23	15
"	" "	360 *	130	108	0	0	26	16	23	15

* No field during irradiation; field applied for 30 minutes after irradiation was stopped.

† % = % Activity.

It is noteworthy that with bromoform the activity is collected indiscriminately on both electrodes, showing that the active bromine in bromoform, unlike the iodine in ethyl iodide, has no characteristic charge, and that its collection on the electrodes is purely a chemical effect. In view of this striking difference in behaviour between bromoform and ethyl iodide, various liquids were tried. Smooth copper electrodes were used, the field being applied during and for 1 minute after irradiation. Newly purchased materials were employed, the colour being

removed, where possible, by standing in contact with copper wire. In some experiments an effort was made to produce ions, in order to facilitate the collection of the active isotope, by passing sulphur dioxide through the liquid. The results are given in Table III and the accompanying notes.

TABLE III.

Smooth copper electrodes; 360-volt field.

Substance.	Kicks/min. Anode.	Kicks/min. Cathode.	Substance.	Kicks/min. Anode.	Kicks/min. Cathode.
Methyl iodide	38	0	Butyl iodide	118	0
Ethyl iodide	100	0	Butyl bromide	70	0
Ethyl bromide	125	0	Ethylene dibromide	88	0

Bromoform: Field has no apparent effect (see above).

Iodobenzene: Always coloured. No activity can be collected even after 30 minutes' passage of sulphur dioxide. The liquid cannot be decolorised by standing over copper wire.

Bromobenzene: The colourless liquid, after standing with copper wire, gave an activity of 35 kicks/min. on the anode and 15 kicks/min. on the cathode. A similar sample, after addition of a trace of bromine and 5 minutes' passage of sulphur dioxide, gave an activity of 28 kicks/min. on each electrode; after addition of sufficient bromine to impart a dark brown colour to the liquid, followed by 30 minutes' passage of sulphur dioxide (conditions analogous to the iodobenzene experiment), no activity was collected on either electrode.

Methylene iodide: Liquid dark brown, and no activity collected even after 30 minutes' passage of sulphur dioxide.

Methylene bromide: Colourless liquid gave all activity on the anode (113 kicks/min.); addition of bromine until liquid was dark brown, and then passage of sulphur dioxide, gave no activity on either electrode.

An interesting feature of the table is that the active bromine in ethyl and butyl bromide and ethylene dibromide, unlike that in bromoform, is collected exclusively on the anode. Methyl bromide, ethylene di-iodide, and iodoform could not be investigated in this way, as the first is a gas and the others are solids.

It seems that no activity is collected on the electrodes in any case where a considerable amount of free halogen is present, and that this absence of activity is due to exchange processes between the active isotope and the excessive quantity of dissolved halogen; *e.g.*, in bromoform, the samples used always had a brown tint which could not be removed by standing with a copper coil. (There would have been no point in trying to remove the colour by distillation, as the experiments with ethyl iodide show that the presence of ions in solution is essential for the collection of the activity on the electrode.) The same explanation is also borne out by the experiments with bromo- and iodo-benzene, and by the fact that in the second experiment described under methylene bromide, a current of the order of 1 m.a. passed through the liquid, showing the presence of ions, and an appreciable deposit of cuprous bromide was left on both electrodes although no activity was collected. In the case of iodobenzene, on the other hand, it is probable that there are no charged particles present, even after passage of sulphur dioxide, as there was an almost complete absence of a deposit on the electrodes and no measurable current passed through the liquid; the non-collection of activity in this case is therefore due to the absence of the minimum amount of ions from which the active isotope, by exchange, could acquire its charge.

From the literature it appears that little is known about the accidental presence of iodine and bromine ions in liquid organic compounds of these halogens. A further investigation was not made of this point, which, however, may be of interest in the study of the mechanism of their reactions.

Investigation of the Behaviour of Ethyl Iodide.—The effect of electrolysing the liquid to zero conductivity had been fouud to be complete removal of colour, and prevention of the collection of any activity on either electrode (see p. 387). Shaking with phosphoric oxide had no effect upon the colour but removed the conductivity. According to Bodenstein and Jost (*J. Amer. Chem. Soc.*, **1927**, **49**, 1416), phosphoric oxide reacts with hydrogen iodide, and it was thought probable that the presence of the latter would prove to be the explanation. Accordingly, experiments were performed upon electrolysed ethyl iodide, colourless and of zero conductivity, the effect being tested of different substances and treatments which might be expected to produce ions in solution. The arrangements were as before, with smooth copper electrodes, and a 360-volt field. The results are summarised in Table IV.

TABLE IV.

Electrolysed ethyl iodide. Smooth copper electrodes; 360-volt field.

Treatment of sample.	Anode. Kicks/min.	Anode. % Activity.	Cathode. Kicks/min.	Cathode. % Activity.	Deposit.
Untreated	0	0	0	0	
10 Days' standing in sunlight	65	54	0	0	
10 Days' standing in dark with Cu wire	85	71	0	0	
Dry HI bubbled through liquid	12	10	0	0	
Crystal of NMe_4I added	25	21	0	0	
Crystal of I_2 added	80	75	10	8	
SO_2 passed	25	21	0	0	Not visible.
Crystal of I_2 added, SO_2 passed	70	58	70	58	
Trace of I_2 added, SO_2 passed	120	100	0	0	Scarcely visible.
Minute trace of I_2 added (not enough to impart a colour to the liquid), and few bubbles of SO_2 passed	65	54	0	0	Not visible.

It will be seen from the table that, in order to obtain a very high concentration factor, with the deposition of a very pure layer of active isotope uncontaminated with inactive material, the best method is to pass a little sulphur dioxide into the electrolysed solution, either with or without the addition of a minute trace of iodine. The presence of too much iodine dilutes the active deposit. Similar efforts to increase the yield of active bromine from bromoform were unsuccessful.

In an endeavour to increase the concentration factor still further, the plate electrodes were replaced by a single-wire anode and a cylindrical copper cathode. The activity on the wire only was measured, but the efficiency of this arrangement was only about one-sixth of that with the plate electrodes (see following table).

Variation in electrodes.

Sample.	Plate anode. Kicks/min.	Plate anode. % Activity.	Wire anode. Kicks/min.	Wire anode. % Activity.
Electrolysed liquid + SO_2	25	21	4	3
Manufacturer's sample, stood with copper wire	85	71	15	12
Electrolysed liquid + trace of I_2 + SO_2	120	100	20	17

Effect of Stirring.—In order to ascertain (*a*) how quickly the active isotope may be collected and (*b*) how long an interval may elapse between interruption of irradiation and collection of the activity, a series of experiments was performed, in which the electrodes were the usual smooth copper plates and the field 360 volts, but the liquid was stirred when required by a mechanical glass stirrer immersed therein. Electrolysed ethyl iodide was used, to which a trace of iodine had been added and through which sulphur dioxide had been passed for 5 minutes. The arrangement of the bath was slightly altered, resulting in diminished activation, but as only comparisons were required, the activity deposited was compared as kicks/minute (allowance being made for incomplete activation and decay) and not as percentages of the total activity obtained by precipitation. The anode activities are given in Table V.

TABLE V.

Effect of stirring electrolysed ethyl iodide + I_2 + SO_2.

Conditions.	Kicks/min.
Field on during irradiation	33
Field on during irradiation + stirring	28
Irradiate without field, remove source, and stir for 2 mins. with field on	24
Irradiate without field, remove source, and have field on for 2 mins. without stirring	15
Irradiate without field, remove source, and stir for ½ min. with field on	15
Irradiate without field, remove source, and have field on for ½ min. without stirring	13
Irradiate without electrodes, then place electrodes in position, and stir with field on for 2 mins. Remove electrodes, and measure activity after 1 hour	14
Irradiate without electrodes, stand for 1 hour, then place electrodes in position, and stir with field on for 2 mins. Measure activity at once	14

It will be seen that stirring during irradiation, with the field on, does not increase the yield. When the field is applied for a short time after irradiation, however, stirring seems to be advantageous.

The experiments involving time intervals necessitated the use of a stronger source, and a 150-mc. radon–beryllium source was employed. The figures are corrected for this and for the decay of the radon source, so comparisons are absolute. It is obvious that the active iodine does not have its charge altered in any way by standing, since the activity on the anode is the same whether the active isotope is collected at once or is allowed to stand and then collected. It was found that the experiments involving stirring always gave a slight activity (about 6 kicks/minute, corrected) on the cathode, even when the field was applied throughout the experiment, but this is not difficult to understand when one recalls that there was evidence in the first few experiments of a definite chemical affinity of the active iodine for the copper electrodes, which must be encouraged by stirring.

Finally, an investigation was made to determine whether the active isotope obtained by the application of an electric field was identical with that obtained by precipitation. It was found that precipitation of all free iodine as silver iodide before irradiation did not affect the collection of the activity on the anode. If, however, the sample was irradiated, sulphur dioxide passed, and the free iodine extracted, no active deposit was collected on the electrodes, even if a trace of iodine and a little sulphur dioxide were added to the liquid after precipitation and before application of the field. This suggests that the active iodine obtained on the electrode is identical with that obtained by precipitation by the method of Szilard and Chalmers (*loc. cit.*), the remaining 40% presumably either never leaving the ethyl iodide molecule or else re-entering it (see following paper).

SUMMARY.

The concentration of artificially produced radio-elements can in many cases be effected by the application of an electric field, for we have found that the active particles are often charged. The radioactive atoms in our experiments were produced by slow neutrons, and the charge acquired by them has nothing to do with the mechanism of the capture of the neutrons, but is due to secondary processes. We have studied in some detail the effects of neutron bombardment on arsine (gaseous phase) and ethyl iodide (liquid phase). The active arsenic isotope ${}^{76}_{33}As$ does not retain any characteristic charge which may be imparted to it at the moment of its formation, but attaches itself to the positive and negative ions present in the gas and can be deposited on electrodes of either sign. In the case of ethyl iodide, the iodine atoms which are activated and, at the same time, detached from the ethyl groups, acquire by exchange processes the negative charge of iodine ions which are usually present in the liquid or, if not, can be easily imparted to it. By electrolysis, therefore, the active isotope ${}^{128}_{53}I$ can be concentrated on a copper or silver anode. By the same method it is possible to collect the active iodine from methyl and butyl iodides and the active bromine from ethyl, butyl, methylene, and ethylene bromides.

From these and other experiments described, it appears that the nature of the secondary processes which lead to the acquisition of electric charges varies, but that frequently the application of an electric field is a good method of obtaining the radioactive isotopes in a practically pure state. The concentration factor in some of our experiments exceeded 20,000.

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92. *Direct Production of Organic Compounds containing Artificial Radio-elements.*

By E. GLÜCKAUF and J. W. J. FAY.

IN view of the increased interest in the use of radioactive indicators for the investigation of biological and chemical reactions (see *e.g.*, Chiewitz and von Hevesy, *Nature*, 1935, **136**, 754; von Hevesy, Lindestrøm, and Olsen, *ibid.*, **137**, 66; Juliusburger, Topley, and Weiss,

J. Chem. Physics, **1935**, **3**, 437), we endeavoured to find new methods for the production of organic compounds with a relatively high percentage of radioactive substance.

After irradiating perchlorate, periodate, and permanganate with slow neutrons, we found, as experiments by Amaldi, d'Agostino, Fermi, Pontecorvo, Rasetti, and Segré (*Proc. Roy. Soc.*, 1935, *A*, **149**, 538) would suggest, that no measurable activity remained in the original molecule, provided that the separation of the ejected active isotope was carried out with sufficient care. On the other hand, it is impossible to remove by aqueous extraction (Szilard and Chalmers, *Nature*, 1934, **134**, 462) or by an electric field (Fay and Paneth, preceding paper) all the active isotope from organic halides, and we found that in such cases between one-half and two-thirds of the activity could not be removed by repeated extraction with a reducing aqueous solution of the corresponding alkali halide. In Fermi's opinion (*loc. cit.*), the energy of the γ-ray recoil is sufficient to eject the active atom from its molecule, and it is therefore probable that the residual activity in organic substances is due to the ejected active atom entering another molecule. In order to be able to separate the minute quantities of any substances likely to be formed as the result of this re-entering process, we added to various organic liquids after irradiation small quantities of the respective isotopic compounds. After extraction of the free halogen, the organic liquid was separated again by distillation or other means into its various components, the activities of which were measured separately on a Geiger–Müller counter. The following is the description of a typical experiment.

32 C.c. (73 g.) of methyl iodide (after addition of a drop of methylene di-iodide and a small crystal of iodine for protection) were irradiated for 1 hour with a 340-mc. radon–beryllium source, the whole being surrounded by water to "slow down" the neutrons. After irradiation, 3 c.c. (10 g.) of methylene di-iodide and 11 c.c. (10 g.) of toluene (the latter to facilitate the separation by distillation of the two halides) were added. The whole was extracted with 46 c.c. (50 g.) of an aqueous solution of potassium iodide and sulphur dioxide. The aqueous extract was separated, 2 c.c. were transferred to a glass vessel with a bottom of aluminium foil (thickness 0·05 mm.), and the activity was measured. A second and a third similar extract were found to contain no measurable activity. The organic liquid was then dried over calcium chloride, and the activity of 2 c.c. of it was measured in a similar vessel. The rest was fractionated and the activities of the components were measured separately. The whole operation can be performed in less than ½ hour. The number of impulses per minute (corrected to zero time) were : 540 for the aqueous extract, 390 for the organic liquid after extraction, 400 for the methyl iodide, 0 for the toluene, 630 for the methylene di-iodide.

In considering these activities, it should be borne in mind that only 32 c.c. of methyl iodide were irradiated. If a larger quantity had been employed, under exactly the same conditions, the activity of the methylene di-iodide would have been several times the value given above. In order to compare the values, a correction must be applied for the concentration and density of the substances measured. We did this approximately by dividing by the ratio of the weight of substance irradiated to the weight of the liquid in which the product under consideration was measured.

The results tabulated below for several experiments show the percentage of the total activity (corrected as above) carried by each constituent.

	Percentage of total activity carried by constituents after separation.			
Substance irradiated.	Aqueous extract (free halogen).	Extracted organic liquid before distillation.	Original substance recovered.	New product found.
CH_3I at 15°	43	57	46	11 (CH_2I_2)
CH_3I at −195°	44	49	45	11 (CH_2I_2)
CH_3I at 15° (with cadmium + boron absorber)	41	55	48	11 (CH_2I_2)
CH_2Br_2	43	64	43	14 ($CHBr_3$)
$CHBr_3$	34	69	47	19 (CBr_4)
C_6H_5Cl	50	50	35	15 ($C_6H_4Cl_2$)
$CH_2Br{\cdot}CO_2H$	78	22	*remained in* aqueous extract	22 (CH_2Br_2)

(Cols. 2, 4, and 5 are made to add up to 100%, and it is seen that, within the limit of experimental error, the sum of cols. 4 and 5 is equal to col. 3.)

The actual percentage of the total activity carried after separation by the new product formed is comparatively small, but it should be remembered that this activity is contained in a small

quantity of substance which, mass for mass, is often many times more active than the original substance irradiated.

By irradiating methyl iodide at liquid-nitrogen temperature, the same result was obtained as in the experiment at room temperature, showing that the production of higher organic halides is not the result of ordinary chemical substitution, which under these conditions would be suppressed. This deduction is supported by the fact that high concentrations of activity were found in the organic substances containing one halogen atom more than the original compounds.

Modified experiments with perchloric acid and methyl iodide were made in order to ensure that the ejection of the active atom was actually produced by the γ-ray recoil and not by the impact of neutrons of medium velocity. The samples were surrounded in both cases by a 5% solution of cadmium chloride, and contained in solution about 5% of cadmium nitrate and methyl borate respectively. In both samples the activity was reduced to one-fifth, showing that at least four-fifths of the original activity was due to the slow neutrons. At the same time the percentages of the total activity carried by the separated constituents were in no way altered (see above table).

That the active halogen atom is always ejected from the molecule is not surprising, in view of the fact that the γ-ray energies already measured for other elements (Rasetti, *Z. Physik*, 1935, **97**, 64) have values between 3·3 and 6·6 $\times$ 10^6 e.v. Even in the case of periodate, in which, the equation $IO_4' \longrightarrow I' + 4O - 270$ cals. being assumed, the iodine has the greatest possible binding energy, the γ-ray energy required to disrupt the bond would be only 1·7 $\times$ 10^6 e.v.

The ability of the activated atoms, ejected from their compounds with high energy, to enter other molecules permits the production of highly active compounds. We were thus able to extract from mixtures newly formed active products as shown below.

Mixtures irradiated.		Products separated with concentrated activity.
$C_2H_5{\cdot}OH + I_2$	(satd.)	CH_3I (6),* C_2H_5I (4).
$CH_3{\cdot}CO_2H + I_2$	(satd.)	CH_3I (10).
$C_6H_6 + CCl_4$	1 : 1	C_6H_5Cl (10).
$C_6H_6 + CBr_4$	1 : 1	C_6H_5Br (15).
$C_6H_5{\cdot}OH + CH_3Br$	1 : 1	CH_3Br (6), C_6H_5Br (2), $C_6H_4Br{\cdot}OH$ (2).
$C_6H_5{\cdot}NH_2,HBr$		C_6H_5Br (1), $C_6H_4Br{\cdot}NH_2$ (2).
$C_6H_6 + CH_3I$	10 : 1	C_6H_5I (15).

* The figures in parentheses denote the approximate percentage of the total activity carried by the constituents.

If one diminishes the possibility of an ejected halogen atom re-entering a molecule by greatly diluting the liquid to be irradiated with an inert substance, no activity should remain in the original liquid after extraction. A 4% solution (by vol.) of bromoform in carbon disulphide was irradiated, and after removal of the free bromine and the carbon disulphide, no measurable activity remained in the bromoform, showing that within the limit of our measurements every halogen atom which captures a neutron is ejected from its molecule. Use was made of this fact in the experiment with benzene and methyl iodide. By using a relatively large amount of benzene, the concentrated activity was obtained mainly as iodobenzene instead of as a mixture of the latter and methylene di-iodide, which would have been difficult to separate. It follows from the last table that the active halogen atom exchanges, not only with halogen or hydrogen, but also with the hydroxyl, amino-, carboxyl, and hydroxymethyl groups and probably many others whenever a stable compound is produced by the exchange.

A continuous supply of organic halides with highly concentrated activities can be obtained by a very convenient method in cases where the original substance irradiated is soluble in water and the product is insoluble and fairly volatile. As an example of the method, 800 c.c. of a saturated solution of potassium iodide in 80% acetic acid were irradiated to equilibrium, and a rapid current of air, saturated with methyl iodide vapour at 0°, was passed through the solution for 5 minutes. The issuing air, after passing through soda–lime and calcium chloride to remove acid and water vapours, was cooled in a U-tube immersed in liquid air, whereby the methyl iodide was frozen out. The liquid air was then removed, and the methyl iodide liquefied and run into one of the glass–aluminium vessels described above. About 1·5 c.c. were obtained, which gave an activity of 5 kicks per minute per mc. five minutes after the air-current had been stopped. By improving the conditions, still higher yields could be obtained. As the composition of the irradiated liquid remains unchanged, the method permits the production of an almost continuous and unlimited supply of active methyl iodide. This particular method of preparation may be of special interest for biological experiments, as most of these volatile organic halides produce anæsthesia and have specific effects on the various parts of the brain.

SUMMARY.

It is shown that when organic halogen compounds are irradiated with slow neutrons, the activated halogen atoms are ejected from their molecules with high energy and then enter other molecules. They replace not only other halogen atoms, but also hydrogen and univalent groups, thereby producing new halogen compounds which can be separated with a high concentration of activity.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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93. *Dipole Moment and Structure of Organic Compounds. Part XV. The Electric Moments of Some Chlorinated Naphthalenes.*

By G. C. HAMPSON and A. WEISSBERGER.

THIS is a continuation of work already published (Weissberger, Sängewald, and Hampson, *Trans. Faraday Soc.*, 1934, **30**, 884) and was undertaken in order to try to settle the following points: (*a*) Is the moment of a substituted naphthalene the same as that of a substituted benzene? (*b*) Is the moment of an α- different from that of a β-substituted naphthalene? (*c*) Is there any evidence from the dipole data of the fixation of double and single bonds in naphthalene? (*d*) Does the introduction of a chlorine atom in one ring have any influence on the other ring?

Existing evidence concerning the structure of naphthalene is confusing. From *X*-ray investigations (Robertson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 674) it appears that naphthalene is centrosymmetric. De Laszlo (*J. Amer. Chem. Soc.*, 1928, **50**, 892), from absorption spectra, concluded that the two neighbouring β-positions (2 and 3) were not quite equivalent to one another, but that positions 2 and 6 were exactly equivalent. From chemical evidence there appears to be a marked difference between the α- and the β-positions, as is shown, *e.g.*, by diazo-coupling to β-hydroxy- and β-amino-naphthalene (see Fieser and Lothrop, *ibid.*, 1935, **57**, 1459, and references therein). According to Pauling and his co-workers (Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362; Sherman, *ibid.*, 1934, **2**, 488), the naphthalene molecule should be considered as a resonance hybrid of 42 canonical structures. Easily the most important are the three unexcited Kekulé-type structures, and of these the symmetrical one, which has a double bond common to both rings, makes a 50% greater contribution to the wave function than either of the two unsymmetrical ones.

The electric moments of a number of naphthalene derivatives have already been measured, but the results in some cases were sufficiently discordant to require a careful redetermination. For all β-substituted derivatives, however, the moment appears to be somewhat larger than that of the α-isomeride, and this led Parts (*Z. physikal. Chem.*, 1930, *B*, **10**, 264) and Nakata (*Ber.*, 1931, **64**, 2059) to conclude that substituents in the β-position in naphthalene are aliphatically bound, or at any rate less aromatically bound than those in the α-position.

For the 1 : 4-, 1 : 5-, and 2 : 6-disubstituted naphthalenes, a moment indistinguishable from zero has been found by some workers, but others have found small but finite moments for some of them (Williams and Fogelberg, *J. Amer. Chem. Soc.*, 1931, **53**, 2069; Bergmann and Engel, *Z. Elektrochem.*, 1931, **37**, 563; Nakata, *loc. cit.*; Weissberger and Sängewald, *Z. physikal. Chem.*, 1933, *B*, **20**, 146; Weissberger, Sängewald, and Hampson, *loc. cit.*). Nakata, for example, found 1 : 5-difluoro- and 1 : 4-dichloro-naphthalene to be non-polar, but 2 : 6-dichloronaphthalene had a small moment, and hence he concluded that the two rings were bent about the common C–C bond.

In cases such as this, where a differentiation between a small moment and one of zero is very important, great care must be taken over the measurement. To obviate the

experimental difficulty of measuring small moments, Nakata used disubstituted derivatives in which the two substituents were different, but owing to the non-additivity of group moments (Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 562) this method cannot be considered satisfactory.

Experimental.

Materials.—α- and β-*Chloronaphthalene* were prepared from the purified amines by the Sandmeyer reaction (Scheid, *Ber.*, 1901, **34**, 1813), followed by steam-distillation, treatment with caustic alkali, and distillation: α-chloronaphthalene, b. p. 255·5—256·0°; β-chloronaphthalene, m. p. 59·5—60·0°.

1 : 6-Dichloronaphthalene was obtained from naphthalene-1 : 6-disulphonyl chloride (Armstrong and Wynne, *Chem. News*, 1890, **62**, 164); m. p. 48—49°. More satisfactory is the preparation from 1 : 6-diaminonaphthalene, obtained in a yield of 72% by reduction of 5-nitro-2-aminonaphthalene (Friedlander and Zsymanski, *Ber.*, 1892, **25**, 2080). The diamine (4·8 g.) was finely dispersed in hydrochloric acid (25 c.c. concentrated acid and 25 c.c. water) and, after cooling in an ice-bath and addition of ice (80 g.), tetrazotised by sodium nitrite (4·2 g.) in water (8 c.c.). The solution was poured into cuprous chloride (20 g.) in concentrated hydrochloric acid (100 c.c.), slowly heated to 60°, filtered, and the residue steam-distilled after addition of caustic soda. The solid distillate had the correct m. p. but was rather yellow; it was therefore dissolved in light petroleum, decolorised (charcoal), the ether evaporated, and the colourless solid recrystallised from alcohol, 1·4 g. (24%) of colourless needles, m. p. 48·5—49·0°, being obtained.

1 : 7-*Dichloronaphthalene*. A sample, for which we thank I. G. Farbenindustrie A.-G., was repeatedly crystallised from benzene and from alcohol, forming colourless needles, m. p. 63·5—64·5°, undepressed on admixture with a specimen for which we are grateful to Professor W. P. Wynne.

1 : 8-*Dichloronaphthalene*. 1 : 8-Diaminonaphthalene (15·8 g.) in hydrochloric acid (80 c.c. conc. acid and 50 g. ice) was quickly tetrazotised and treated with cuprous chloride under conditions parallel to the above, benzene being added to prevent formation of froth. The mixture was slowly heated to boiling until the benzene was distilled off, then steam-distilled, and the solid distillate triturated in the cold with aqueous potassium hydroxide, filtered off, and steam-distilled after addition of caustic potash. The solid distillate was recrystallised from alcohol (11·9 g., 59%), colourless needles, m. p. 87—89°, and finally from hexane, m. p. 89·0—89·5°.

2 : 3-*Dichloronaphthalene*. We thank Messrs. Imperial Chemical Industries Ltd. for a pure sample (m. p. 119·5—120·5°) which gave no depression in m. p. with a specimen kindly supplied by Professor W. P. Wynne.

The other dichloronaphthalenes were either identical with, or prepared by the same methods as, the substances described in previous papers (Weissberger and Sängewald; Weissberger, Sängewald and Hampson, *locc. cit.*).

Measurements.—The data for the determination of dipole moments are in the following tables, where the symbols have their usual significance. All the measurements were carried out in benzene solution at 25·0°.

f_2.	d.	ϵ.	n^2.	P_2.	$_EP_2$.
		α-Chloronaphthalene.			
0·029580	0·8882	2·3878	2·27775	97·11	50·24
0·019137	0·8833	2·3464	2·27008	96·80	49·76
0·011181	0·8795	2·3160	2·26542	97·18	50·14
0·010505	0·8792	2·3133	2·26531	97·15	50·69
		1 : 2-Dichloronaphthalene.			
0·018511	0·8879	2·4426	2·27302	174·8	55·43
0·013853	0·8844	2·4007	2·26929	176·5	55·43
0·006468	0·8787	2·3330	2·26375	179·5	56·84
		1 : 5-Dichloronaphthalene.			
0·010398	0·8815	2·2809	2·26661	55·20	55·54
0·009691	0·8810	2·2808	2·26586	55·57	55·16
0·005454	0·8777	2·2766	2·26244	54·16	55·39

f_2.	d.	ϵ.	n^2.	P_2.	$_EP_2$.
		β-Chloronaphthalene.			
0·023294	0·8848	2·3765	2·27285	105·75	50·27
0·018187	0·8825	2·3539	2·26975	105·95	50·31
0·008761	0·8781	2·3118	2·26361	106·27	50·27
		2 : 3-Dichloronaphthalene.			
0·013535	0·8841	2·4059	2·26808	185·08	54·51
0·010262	0·8816	2·3730	2·26537	184·95	54·20
0·007617	0·8796	2·3476	2·26361	186·40	54·47
0·006162	0·8785	2·3334	2·26248	186·95	54·32
		1 : 3-Dichloronaphthalene.			
0·010688	0·8818	2·3289	2·26641	120·9	55·56
0·008536	0·8802	2·3179	2·26466	121·5	55·45
0·008244	0·8798	2·3154	—	120·6	—

f_2.	d.	ϵ.	n^2.	P_2.	${}_EP_2$.
1 : 4-Dichloronaphthalene.					
0·013770	0·8841	2·2879	2·26860	59·80	54·63
0·010420	0·8816	—	2·26632	—	55·00
0·008659	0·8802	2·2823	2·26503	59·80	55·19
0·006439	0·8785	2·2797	2·26295	59·40	54·51
1 : 7-Dichloronaphthalene.					
0·013909	0·8842	2·5072	2·26811	183·4	54·96
0·013005	0·8835	2·3993	2·26735	184·6	54·96
0·007796	0·8798	2·3483	2·26372	184·9	54·93
0·005295	0·8779	2·3251	2·26185	188·4	54·88
2 : 6-Dichloronaphthalene.					
0·015300	0·8851	2·2842	2·26932	55·64	55·20
0·013413	0·8837	2·2828	2·26794	55·71	55·27
0·012634	0·8831	2·2824	2·26740	55·87	55·26
0·010410	0·8814	2·2806	2·26570	55·95	55·42

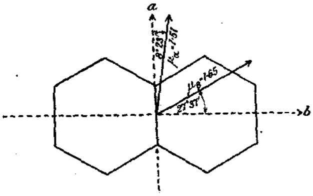
f_2.	d.	ϵ.	n^2.	P_2.	${}_EP_2$.
1 : 6-Dichloronaphthalene.					
0·014161	0·8848	2·3239	—	97·35	—
0·011094	0·8825	2·3126	—	97·26	—
0·008394	0·8805	2·3031	—	97·56	—
0·014416	0·8846	—	2·26831	—	54·73
0·012975	0·8836	—	2·26720	—	54·62
0·011299	0·8740	—	2·26621	—	54·93
1 : 8-Dichloronaphthalene.					
0·022350	0·8912	2·5337	2·27637	206·8	55·90
0·018215	0·8879	2·4863	2·27305	208·9	55·11
0·009633	0·8812	2·3870	2·26598	213·9	55·28
0·007927	0·8798	2·3682	2·26455	217·2	55·35
2 : 7-Dichloronaphthalene.					
0·012554	0·8831	2·3212	2·26706	101·17	55·03
0·011712	0·8825	2·3192	2·26664	102·69	55·24
0·008653	0·8803	2·3071	2·26446	102·88	55·43
0·005546	0·8779	2·2948	2·26185	103·23	54·81

Substance.	P_2.	${}_EP_2$.	${}_{A+O}P_2 = P_2 - {}_EP_2$.	μ, D.
1-Chloronaphthalene	97·5	50·2	47·3	1·51
2-Chloronaphthalene	106·6	50·3	56·3	1·65
1 : 2-Dichloronaphthalene	181·9	55·4	126·5	2·47
1 : 3-Dichloronaphthalene	121·0	55·5	65·5	1·78
1 : 4-Dichloronaphthalene	59·7	54·9	4·8	0·48
1 : 5-Dichloronaphthalene	55·1	55·3	—	0
1 : 6-Dichloronaphthalene	97·8	54·8	43·0	1·44
1 : 7-Dichloronaphthalene	189·5	54·9	134·6	2·55
1 : 8-Dichloronaphthalene	220·0	55·2	164·8	2·82
2 : 3-Dichloronaphthalene	189·0	54·4	134·6	2·55
2 : 6-Dichloronaphthalene	55·8	55·3	—	0
2 : 7-Dichloronaphthalene	103·5	55·1	48·4	1·53

Discussion.

Concerning the sources of error inherent in the method used, it would appear that atom polarisation in this series of compounds is negligible. The difference between P_2 and ${}_EP_2$ for 1 : 5- and 2 : 6-dichloronaphthalene, which one would expect to be non-polar, is certainly less than 1 c.c., and a similar small difference has been found for naphthalene itself (Parts, *loc. cit.*). The other source of error is the solvent effect, and since all these substances were measured in one solvent under the same conditions the results are probably strictly comparable (Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945).

FIG. 1.



Significance of Results.—Since the moments of 1 : 5- and 2 : 6-dichloronaphthalene are zero within the experimental error, the small value found for the 1 : 4-derivative has some significance and indicates that the moment of an α-substituted naphthalene is not quite parallel to the *a*-axis of the naphthalene molecule (see Fig. 1). This could arise either if the α-substituent itself were not directed as from the centre of the ring, or if this substituent were so directed, but induced a moment in the rest of the molecule which had a component along the *b*-axis. Also, the difference in moment of the α- and β-monochloronaphthalenes can be explained either by the moment of the C–Cl link in the two positions being different, or by a polarisation of the rest of the molecule by this link (Weissberger, Sängewald, and Hampson, *loc. cit.*).

In order to determine the direction of the resultant moment of the α- and the β-monochloro-derivatives relative to the *a*- and the *b*-axis of the naphthalene molecule, consider

that these resultants are each made up of two components along these principal axes. This introduces four unknowns which can be determined by solving four equations set up from four of the measurements. Besides the two monochloro-derivatives, the two dichloro-derivatives chosen for setting up these equations were the 1 : 6- and the 2 : 7-compound, since in these the chlorine atoms are far apart and so the Smallwood–Herzfeld effect (*J. Amer. Chem. Soc.*, 1930, **52**, 1919) is negligible. Of course, this method of treatment presupposes that the moment of the disubstituted compound is the vector sum of the component moments of the monosubstituted compounds. This assumption is probably not strictly correct, but if the result which it gives enables the values of the moments of the other dichloronaphthalenes to be calculated correctly, then one is justified in using this method.

If the component moments along the a and the b axis for the α-compound are x and y, and for the β-compound p and q, the equations are

$$x^2 + y^2 = 1{\cdot}51^2 \qquad p^2 + q^2 = 1{\cdot}65^2$$
$$2p = 1{\cdot}53 \qquad (a - p)^2 + (q - b)^2 = 1{\cdot}44^2$$

from which $x = 1{\cdot}494$, $y = 0{\cdot}22$, $p = 0{\cdot}765$, $q = 1{\cdot}462$. In other words the measured moments 1·51 and 1·65 of α- and β-monochloronaphthalene are inclined at angles 8°23′ and 27°37′ to the principal axes of the naphthalene molecule, as shown in Fig. 1. Using these values to calculate the moments of the other dichloronaphthalenes, we obtain the results shown below.

Substance.	$\mu_{calc.}$	$\mu_{obs.}$	$\mu_{obs.}/\mu_{calc.}$
1 : 7-Dichloronaphthalene	2·57	2·55	0·99
1 : 3-Dichloronaphthalene	1·83	1·78	0·97
1 : 8-Dichloronaphthalene	2·99	2·82	0·94
1 : 2-Dichloronaphthalene	2·82	2·47	0·87
2 : 3-Dichloronaphthalene	2·92	2·55	0·87
1 : 4-Dichloronaphthalene	0·44	0·48	0·92

The small difference between $\mu_{obs.}$ and $\mu_{calc.}$ for the 1:4-compound is, of course, meaningless in a moment of this magnitude. Of the others, the differences can all be explained by a Smallwood–Herzfeld effect, the ratio of $\mu_{obs.}/\mu_{calc.}$ approaching unity as the distance apart of the two chlorine atoms increases. The value of $\mu_{obs.}/\mu_{calc.}$ for 1:2- and 2:3-dichloronaphthalene might be expected to be the same as that of $\mu_{obs.}/\mu_{calc.}$ for 1:2-dichlorobenzene. The value of the latter is 0·86 (from Müller's polarisation data, *Physikal. Z.*, 1933, **34**, 689). Similarly, the value of $\mu_{obs.}/\mu_{calc.}$ for 1 : 3-dichlorobenzene is 0·97, in agreement with the value found for 1 : 3-dichloronaphthalene.

It would appear, therefore, that this method of treatment is satisfactory, and it remains now to try to explain the difference in the moments of α- and β-monochloronaphthalenes.

One possibility (Weissberger, Sängewald, and Hampson, *loc. cit.*) is that the C–Cl moment is the same in the two positions and is directed as from the centre of the ring, but that, in addition, the substituent sets up an induced moment in the system which is directed from the unsubstituted ring. This problem has since been discussed by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 188), and we are indebted to him for his helpful advice.

A monosubstituted naphthalene molecule may be regarded as a substituted benzene molecule to which a polarisable system has been attached. This system consists of four aromatic C–H groups, and its polarisability α has been assumed to be two-thirds of that of a benzene ring. This is justified, since the aromatic character of the ring is preserved. The moment μ of the substituent will induce moments μ_x and μ_y at the mass centre of this polarisable system, μ_x and μ_y being respectively parallel and perpendicular to the inducing moment μ (see Figs. 2 and 3). Now μ_x and μ_y are respectively equal to $\{(\varepsilon + 2)/3\}\alpha E_x$ and $\{(\varepsilon + 2)/3\}\alpha E_y$, ε being the dielectric constant of the medium and E_x and E_y being the components of the field in the directions x and y. Also, since E_x and E_y are respectively equal to $\mu(3\cos^2\Theta - 1)/\varepsilon r^3$ and $\mu . 3\sin\Theta\cos\Theta/\varepsilon r^3$ (Frank, *loc. cit.*, p. 176), μ being the inducing moment, r the distance between the inducing moment and the polarisable centre, and Θ the angle between the directions of μ and r, then μ_x and μ_y can be evaluated in terms of ε, α, μ, Θ, and r. In order to determine r, it is necessary to locate the position of

the inducing dipole; this cannot be done with certainty, but in the following calculations it is assumed to be at the point of contact of the carbon and the chlorine atoms. Using as standard data throughout $\epsilon = 2{\cdot}27$, $\mu = 1{\cdot}55$, $\alpha = 2/3 \times 12{\cdot}5 \times 10^{-24} = 8{\cdot}33 \times 10^{-24}$,* and $C_{ar.}$–$C_{ar.}$ = 1·40 Å., we obtain the following results.

	r, Å.	Θ.	μ_x.	μ_y.
α-Chloronaphthalene	3·69	55°17′	−0·004 *	0·226
β-Chloronaphthalene	4·96	17°47′	0·114	0·058

* *I.e.*, in the opposite direction to that shown in Fig. 2.

Taking into account these induced moments, one calculates that the resultant moments of α- and β-chloronaphthalene are 1·56 and 1·66, respectively, inclined at angles of 8°19′ and 28° to the *a*- and the *b*-axis of the naphthalene molecule. These results are in good agreement with those deduced on p. 396 from the experimentally determined dipole data. It follows that the moment of 1 : 4-dichloronaphthalene can be completely explained by a polarisation effect of the two C–Cl moments on the unsubstituted ring (moment : calc., $2\mu_y = 0{\cdot}45$; obs. = 0·48) and that the difference in moment of α- and β-chloronaphthalene, as also that between those of the 1 : 6- and 2 : 7-, and the 1 : 2- and 2 : 3-dichloronaphthalenes, can be explained by the different polarising influence of the C–Cl bond in the α- and the β-position.

Fig. 2.
α-Chloronaphthalene.

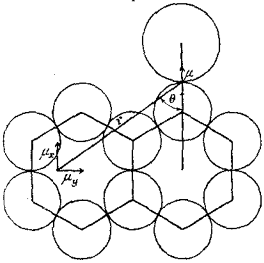
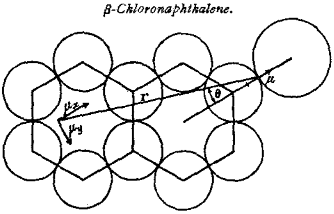


Fig. 3.
β-Chloronaphthalene.



In these calculations it has been assumed throughout that the C–Cl moment in chloronaphthalene is 1·55, and by using this the value of 1·56 was deduced for the moment of α-chloronaphthalene. The experimental value is 1·51, and the discrepancy is rather outside the limits of experimental error. The explanation may be that the C–Cl moment in the α- is less than in the β-position, *i.e.*, in the α-position there is a greater mesomeric effect into the ring. This would be in accordance with the different chemical properties of α- and β-substituted naphthalenes, and also with the observation that the dissociation constant of α- is greater than that of β-naphthol.

If the polarisation theory developed above is correct, it should of course be applicable to other similar systems. Such a one is the series pyridine, quinoline, *iso*quinoline, acridine. The available dipole data (Rolinski, *Physikal. Z.*, 1928, **29**, 658; Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446; Le Fèvre and Smith, J., 1932, 2810; Le Fèvre and Le Fèvre, J., 1935, 1470) are reasonably concordant for this series of compounds, the order of the moments being *iso*quinoline > pyridine > quinoline > acridine. In applying calculations similar to those on p. 396 for the chloronaphthalenes, it is still more difficult in this case to locate the position of the inducing dipole, but qualitatively, at any rate, the theory predicts the above sequence. Similarly, the differences in moment between pyrrole, indole, and carbazole (Cowley and Partington, this vol., p. 47) can no doubt also be accounted for by this polarisation effect.

* For the value of the polarisability of benzene in the plane of the ring ($12{\cdot}5 \times 10^{-24}$), see Debye, "Handbuch der Radiologie," Vol. 6, p. 786, Leipzig, 1925, and Landolt–Börnstein–Roth, 5th ed.

CONCLUSIONS.

(1) Each C–Cl bond in the chloronaphthalenes is directed as from the centre of the ring; if there is any fixation of the single and the double bonds in naphthalene it is not revealed in the direction of the substituents (see Mills and Nixon, J., 1930, 2510).

(2) When a chlorine atom is substituted in the β-position in naphthalene, the C–Cl moment is the same, or very nearly the same, as in chlorobenzene. In the α-position it may be a little less, indicating a greater mesomeric effect into the ring.

(3) The moments of all the mono- and di-chlorinated naphthalenes can be accounted for on the basis of (1) and (2) if an additional polarisation effect is taken into account, the polar group inducing a moment in the rest of the system according to the polarisability of the system. In the dichloronaphthalenes, when the two chlorine atoms are close together, a part of this polarisation effect is a mutual effect of the two C–Cl bonds upon one another, *i.e.*, the well-known "ortho-effect" discussed by Smallwood and Herzfeld. In the ortho-positions there may also be a steric factor.

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THE DYSON PERRINS LABORATORY, OXFORD. [*Received, February 3rd*, 1936.]

NOTES.

Identification of Acids and Esters. By DOUGLAS V. N. HARDY.

ESTERS may be directly converted into the corresponding anilides by treatment with anilinomagnesium bromide (Bodroux, *Compt. rend.*, 1904, **138**, 1427; 1906, **142**, 401; *Bull. Soc. chim.*, 1905, **33**, 832), which is readily obtained from any simple Grignard reagent and aniline. By replacement of the latter with other aromatic amines, substituted anilides may also be obtained:

$$R{\cdot}NH_2 + R'MgX \longrightarrow R{\cdot}NH{\cdot}MgX + R'H$$

$$2R{\cdot}NH{\cdot}MgX + R''{\cdot}CO{\cdot}OR''' \longrightarrow R''{\cdot}C(O{\cdot}MgX)(NHR)_2 \xrightarrow{H_2O} R''{\cdot}CO{\cdot}NHR + R{\cdot}NH_2 + HO{\cdot}MgX$$

This process for identifying the acidic component of an ester is speedy, economical, and employs materials which are generally available. It is particularly valuable when used in conjunction with the separation of acid mixtures by fractional distillation of the corresponding methyl or other ester (cf. Hardy, this vol., pp. 362, 364). Even when small, the individual fractions may be readily converted into anilides in order to identify the original acids. If necessary, an identification may be confirmed by a similar preparation of a substituted anilide. The experimental procedure is as follows: Aniline (4 g.) is slowly dropped into a cold solution of ethylmagnesium bromide prepared from magnesium (1 g.), ethyl bromide (5 g.), and pure dry ether (30 c.c.). When the vigorous evolution of ethane has ceased, the ester (0·02 mol.) is added, the mixture warmed on a water-bath for 10 minutes and cooled, and dilute hydrochloric acid added to dissolve magnesium compounds and the excess of aniline. After removal of ether the anilide, which is obtained in almost calculated amonnt, remains as a solid crust above the aqueous solution.

Thanks are due to Professor G. T. Morgan, Director of Chemical Research, for permission to publish this note.—CHEMICAL RESEARCH LABORATORY, TEDDINGTON. [*Received, February 5th*, 1936.]

A Minimum Estimate of the Dipole Moments of Two Oxonium Salts. By (Mrs.) C. G. LE FÈVRE and R. J. W. LE FÈVRE.

THE pyrylium, flavylium, and xanthylium salts have been considered by Robinson to be oxonium salts with the positive charge distributed over the C–O–C atoms of the kation. Direct physical proof of this has been difficult owing to the limited solubilities of these substances in suitable solvents. The following compounds have been found to dissolve in dimethylaniline: 2-Phenyl- and 2-phenyl-3-methylbenzopyrylium perchlorates, 2-phenyl-, 6-chloro-2-phenyl-, and 6 : 8-dichloro-2-phenyl-benzopyrylium ferrichlorides, and 4-phenyl-2 : 6-di-*p*-tolylpyrylium ferrichloride. Of these, the polarisations of only the first two were successfully determined, because the others gave solutions having such high conductivities that the measurement of their dielectric constants by the resonance method was impossible.

Observations.—The symbols in the following tables have already been defined (J., 1935, 959)

2-Phenylbenzopyrylium perchlorate in dimethylaniline at 25°.

$f_1 . 10^6$	0	833·0	1399·9	1603·9	2113·1
ϵ	4·8435	4·9589	5·0397	5·0455	5·1090
d	0·95198	0·95280	0·95336	0·95357	0·95409
P_1	—	1216·7	1226·8	1103·1	1091·7
n	1·55971	—	—	—	1·56023
R_1	—	—	—	—	75·9

Whence P_1 for $f_1 = 0$ is *ca.* 1250, and μ = *ca.* 8.

2-Phenyl-3-methylbenzopyrylium perchlorate in dimethylaniline at 25°.

$f_1 . 10^6$	0	1500·1	2066·9	2998·7	3802·5
ϵ	4·8435	5·0135	5·0866	5·1828	5·2651
d	0·95198	0·95350	0·95394	0·95500	0·95558
P_1	—	1014·2	1042·4	992·7	970·4

Whence P_1 for $f_1 = 0$ is *ca.* 1100, and μ = *ca.* 7.

These are probably only minimum estimates, since if it were possible to effect measurements at higher dilutions than those employed, the polarisations at infinite dilution would undoubtedly appear to be much larger. Nevertheless, the order obtained is that to be expected if an electron is transferred in a molecule through a distance of 1·5 Å. For comparison, it is recorded that Wrede (*Z. Physik*, 1927, **44**, 261), using the molecular-beam method, found μ = *ca.* 10 for certain alkali halides, Malone and Ferguson (*J. Chem. Physics*, 1934, **2**, 99) reported 7·84 for lithium perchlorate in dioxan, and Williams (*J. Amer. Chem. Soc.*, 1928, **50**, 2350) 4·7 for silver perchlorate in benzene solution at 25°. The last determination was repeated by Kraus and Hopper (*ibid.*, 1934, **56**, 2265), using much lower concentrations, and a limiting molecular polarisation of the order 2,000 c.c. was found, corresponding to a moment considerably higher than that reported by Williams.—UNIVERSITY COLLEGE (UNIVERSITY OF LONDON). [*Received, November* 28*th*, 1935.]

Telfairic Acid. By GEORGE D. GOODALL and ROBERT D. HAWORTH.

THOMS (*Arch. Pharm.*, 1900, **238**, 48) isolated an isomeride of linoleic acid, which he named telfairic acid, from the seeds (Koeme seeds) of *Telfairia pedata*. A re-examination of this acid, rendered possible in 1930 by the kindness of Dr. R. S. Morrell, to whom our thanks are due for a supply of seeds, has shown that telfairic acid is identical with linoleic acid.

The kernels of the seeds on extraction with light petroleum (b. p. 40—60°) gave a 60% yield of a pale yellow oil (iodine value, 89·0; saponification value, 192·5). This oil (50 g.) was saponified with 10% methyl-alcoholic potassium hydroxide (200 c.c.), and the acids, liberated with 10% sulphuric acid, were isolated with ether. The unsaturated acids (35 g.), separated by the lead salt–ether method and subjected to Rollett's bromination process (*Z. physiol. Chem.*, 1909, **62**, 410), yielded tetrabromostearic acid (15 g.), m. p. 114° after crystallisation from light petroleum (b. p. 60—80°), which gave no depression in m. p. with an authentic specimen. Methyl tetrabromostearate, m. p. 58°, and tetrahydroxystearic acid, m. p. 174°, were prepared and identified by comparison with authentic specimens obtained from poppy-seed oil.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [*Received, January* 21*st*, 1936.]

Velocity of the Reaction between o-*Nitrobenzyl Bromide and Pyridine. Addendum to Mechanism of Aromatic Side-chain Reactions, etc. Part IV.* By JOHN W. BAKER.

IT was suggested by Bennett (*Chem. and Ind.*, 1935, **54**, 1008) that the increased velocity of reaction of 2 : 4-dinitrobenzyl bromide with pyridine (in dry acetone) (J., 1935, 1840) might be due to the electron repulsion by the negatively charged oxygen of the *o*-nitro-group acting directly, through the medium, on the side-chain bromine. *o*-Nitrobenzyl bromide has now been investigated, and the velocity is compared below with those observed for benzyl bromide and its *p*-nitro- and 2 : 4-dinitro-derivative.

Interaction of $R{\cdot}C_6H_4{\cdot}CH_2Br$ *and Pyridine in Dry Acetone at* 40° (0·025M).

R =	H.	*o*-NO_2.	*p*-NO_2.	2 : 4-$(NO_2)_2$.
$k \times 10^4$, sec.$^{-1}$	4·817	5·47	4·333	8·960

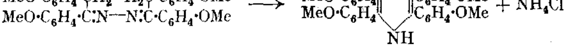
The slight acceleration produced by the *o*-nitro-substituent indicates that a small direct effect in the above sense must be recognised. Since a *p*-nitro-group has a small retarding influence, the much greater velocity increase observed in the 2 : 4-dinitro-compound cannot, however, be

accounted for on this basis. As suggested (*loc. cit.*), the latter increase must result from the greatly increased electron attraction due to the presence of two nitro-groups appropriately oriented to the side chain.

The value of $k \times 10^4$ for the *o*-compound at 20° is 1·33, whence E (Arrhenius) is 12,870 cals., a value closely similar to those obtained for other members of the series.—THE UNIVERSITY, LEEDS. [*Received, January 25th*, 1936.]

Tetra-anisylpyrrole. By F. E. KING and G. D. PATERSON.

FOR the purposes of an investigation requiring an easily accessible hydroxyaryl derivative of pyrrole, the method introduced by G. M. and R. Robinson (J., 1918, **113**, 639) for the preparation of tetraphenylpyrrole was extended to the synthesis of the *tetra-anisyl* compound (I). Cyclisation of the necessary intermediate, *viz.*, the *azine* of deoxyanisoin, occurred as follows:



(I.)

When demethylated, the pyrrole (I) yielded tetra-*p*-hydroxyphenylpyrrole, which was characterised as an *acetate*. The free hydroxy-compound is readily attacked by air and all the usual oxidising agents, but no crystalline products were isolable.

Anisyl p-*Methoxybenzyl Ketazine.*—The requisite ketone was prepared by reducing anisoin with hydrochloric acid and stannous chloride in alcohol (Apitzsch and Metzger, *Ber.*, 1904, **37**, 1676), a process which renders it more readily available than deoxybenzoin (see Apitzsch, *ibid.*, 1907, **40**, 1803). When heated with phenylhydrazine at 120° until evolution of steam had ceased, it gave a *phenylhydrazone*, which slowly crystallised from a little methyl alcohol in needles, m. p. 79°, that subsequently darkened (Found: C, 76·5; H, 6·5. $C_{22}H_{22}O_2N_2$ requires C, 76·3; H, 6·3%).

Following the preparation of phenyl benzyl ketazine (G. M. and R. Robinson, *loc. cit.*), deoxyanisoin (4 g.) in alcohol (60 c.c.) was boiled under reflux with a solution of hydrazine sulphate (0·8 g.) and sodium acetate (5 g.) in water (40 c.c.). Precipitation of the *azine*, which began after 1 hour, was complete in 5 hours; the solution was then cooled, and the product (3·6 g.) collected. Crystallisation from large volumes of ethyl acetate gave orange-yellow needles, m. p. 155° (Found: N, 5·3. $C_{32}H_{32}O_4N_2$ requires N, 5·5%).

Tetra-anisylpyrrole.—Over the surface of the molten ketazine (15 g.), heated in an oil-bath at 170° and periodically shaken, a slow stream of hydrogen chloride was passed for 1 hour. The resulting *tetra-anisylpyrrole* (11 g.) was isolated by extracting the product with boiling acetic acid and filtering it from ammonium chloride. It was readily soluble in hot alcohol and ethyl acetate, but was best crystallised from acetic acid; although the solutions were usually green, by washing with a little methyl alcohol, colourless needles, m. p. 184°, were obtained (Found: C, 78·3; H, 5·9. $C_{32}H_{29}O_4N$ requires C, 78·2; H, 5·9%). The pyrrole dissolved in concentrated sulphuric acid to a red-brown solution with a dark green reflex, the colour eventually becoming olive-green.

Tetra-p-*hydroxyphenylpyrrole.*—When redistilled hydriodic acid (20 c.c.) was refluxed (oil-bath at 140°) with tetra-anisylpyrrole (3 g.) in a carbon dioxide atmosphere for 1½ hours, smooth and complete demethylation occurred. The insoluble product (2·5 g.) was collected, washed with water containing sulphur dioxide, and freed from iodine by shaking a solution in ethyl acetate with aqueous thiosulphate. By the addition of light petroleum to the dried solution, tetra-*p*-hydroxyphenylpyrrole was precipitated in minute colourless needles, m. p. 290° with previous decomposition, but owing to fairly ready atmospheric oxidation satisfactory analytical figures were unobtainable. It was therefore converted into the *acetyl* derivative by heating with anhydrous sodium acetate and excess of acetic anhydride under reflux (oil-bath at 160°) for 2 hours and isolated by pouring the solution into water. The product, which was insoluble in alcohol, crystallised from ethyl acetate in rosettes of colourless needles, m. p. 195° after softening at 150—160°. Drying in a vacuum at 130°, however, led to a slight loss in weight, and fusion then occurred at 195° without previous softening (Found, with dried material: C, 71·4; H, 4·9. $C_{36}H_{29}O_8N$ requires C, 71·6; H, 4·8%).

The authors thank Imperial Chemical Industries, Ltd., for grants.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, January 27th*, 1936.]

94. *Grignard Reactions with Ethyl β-Chloropropionate. Part I.*

By Ch. Weizmann and Ernst Bergmann.

For the synthesis of amino-alcohols containing side chains, a method has been devised starting with ethyl β-chloropropionate. This reacts with Grignard compounds, giving β-chloroethyldialkylcarbinols, which condense easily with secondary amines, yielding, *e.g.*, with piperidine, β-piperidinoethyldialkylcarbinols. By treatment with alcoholic potash, hydrogen chloride is split off, with formation of dialkylvinylcarbinols. The *dibenzylvinylcarbinol* thus obtained from *dibenzyl-β-chloroethylcarbinol* gives, on catalytic hydrogenation, *dibenzylethylcarbinol* identical with the carbinol obtained by interaction of dibenzyl ketone and ethylmagnesium bromide.

Dehydration of the carbinols, saturated or unsaturated, could not be effected smoothly. The product of the reaction between ethyl β-chloropropionate and phenylmagnesium bromide, however, underwent spontaneous dehydration, yielding *γγ-diphenylallyl chloride*. When this was treated with phenylmagnesium bromide, it gave αα-diphenyl-β-benzylethylene, the structure of the chloro-compound thus being proved (compare Meisenheimer, *Annalen*, **1927**, **456**, 151). Besides γγ-diphenylallyl chloride, a small amount of β-chloropropiophenone was formed in the above Grignard reaction; it could not be isolated in a pure state, but its presence was proved by treatment with phenylmagnesium bromide, which gave β-phenylpropiophenone.

Experimental.

Dibenzyl-β-chloroethylcarbinol.—A Grignard solution prepared from magnesium (16·25 g.) and benzyl chloride (77 c.c.) was added drop by drop to a cold ethereal solution of ethyl β-chloropropionate (42 c.c.). After 2 hours' heating on the water-bath, the mixture was poured into ice-cold dilute sulphuric acid; the ethereal layer was washed with sodium carbonate solution, dried, and evaporated. The residual *carbinol* (35—46 g.) had b. p. 214°/22 mm., 206°/8 mm., 192°/3 mm. (Found: C, 74·2; H, 7·2. $C_{17}H_{19}OCl$ requires C, 74·4; H, 7·0%). After it (10 g.) had been heated with potassium hydrogen sulphate (5 g.) at 180—190° for 2 hours, it was recovered mostly unchanged; only a small amount of a lower-boiling fraction was obtained, which did not give satisfactory analytical figures.

Dibenzylvinylcarbinol.—The preceding chloro-compound (13·7 g.) in methyl alcohol (10 c.c.) was left at the ordinary temperature with 20% methyl-alcoholic potash (14 c.c.) for 12 hours. The liquid was then boiled for 6 hours, the methyl alcohol distilled off, and the residue neutralised with sulphuric acid and treated with water and ether. From the latter, *dibenzylvinylcarbinol* was isolated as a yellowish oil (6 g.), b. p. 145—146°/1 mm. (Found: C, 86·2; H, 7·7. $C_{17}H_{18}O$ requires C, 85·8; H, 7·6%).

Dibenzylethylcarbinol.—(a) The above unsaturated carbinol (5·7 g.) in boiling propyl alcohol (30 c.c.) was treated with hydrogen in presence of palladised barium sulphate (3 g.) for 3 hours. The solution was then filtered and evaporated, and the residue distilled, yielding *dibenzylethylcarbinol*, b. p. 190—192°/12 mm., $n_D^{20°}$ 1·5593 (Found: C, 84·8; H, 8·0. $C_{17}H_{20}O$ requires C, 85·0; H, 8·3%). (b) Dibenzyl ketone (10·5 g.) was treated with ethylmagnesium bromide (ethyl bromide, 6 g., and magnesium, 1·4 g.). The product (7·5 g.) had b. p. 197—200°/17 mm., $n_D^{20°}$ 1·5599 (Found: C, 84·7; H, 8·0%).

Dibenzyl-β-piperidinoethylcarbinol.—A mixture of dibenzyl-β-chloroethylcarbinol (14 g.) and piperidine (10 c.c.) was heated at 100° in a sealed tube for 5 hours, the crystalline mass treated with ether and water, the ethereal solution shaken with dilute hydrochloric acid, and the extract made alkaline and again shaken with ether. The *piperidino-carbinol* (9 g.) was obtained as an oil, b. p. 224—225°/5 mm., which readily solidified; m. p. 45—46° (Found: C, 82·0; H, 9·0. $C_{22}H_{29}ON$ requires C, 81·7; H, 8·9%).

The p-*nitrobenzoate*, prepared by heating the piperidino-carbinol (9 g.) and *p*-nitrobenzoyl chloride (5·2 g.) in benzene (50 c.c.) and pyridine (2·2 c.c.) for 3 hours, crystallised from alcohol in diamond-shaped prisms (8·5 g.), m. p. 138—139° (Found: N, 6·2. $C_{29}H_{32}O_4N_2$ requires N, 5·9%).

The *p*-aminobenzoate was prepared by treating the *p*-nitrobenzoate (7 g.) in hot alcohol with alcoholic sodium hydrosulphide (2 g.), added in small portions, and boiling the whole for 1 hour. The alcohol was evaporated, and the residue treated with water and ether. The product was a resin which crystallised immediately after distillation (b. p. 245—250°/25 mm.). The crystals

were triturated with methyl alcohol and recrystallised from propyl alcohol, forming leaflets, m. p. 147—148°.

β-*Chlorotriethylcarbinol*.—This was prepared by the method described above, ethyl bromide (57·2 c.c.) being used in place of benzyl chloride. It boiled at 118—119°/54 mm. (yield, 19—25 g.), and had a pleasant smell (Found: C, 56·3; H, 9·8. $C_7H_{15}OCl$ requires C, 56·0; H, 10·0%). When it was heated with *p*-nitrobenzoyl chloride in benzene and pyridine, *p*-nitrobenzoic anhydride was obtained, m. p. 187° (from toluene).

β-*Piperidinotriethylcarbinol*.—The preceding carbinol (28 g.) was treated with piperidine (40 c.c.) as described above. The *product* (18 g.) had b. p. 105—106°/3 mm. (Found: C, 72·3; H, 12·5. $C_{12}H_{25}ON$ requires C, 72·4; H, 12·6%).

When the piperidino-carbinol (5·5 g.) was treated with *p*-nitrobenzoyl chloride as described above, a thick crystalline mass of the hydrochloride of the expected compound (thus proved to be more basic than pyridine!) was obtained. It was treated with alkali, and the crystalline product recrystallised from alcohol; it separated with alcohol of crystallisation (m. p. 100°), but lost this even at room temperature (m. p. 148°).

β-*Chloroethyldibutylcarbinol*, prepared from ethyl β-chloropropionate (41 g.), magnesium (11 g.), and butyl bromide (90 g.; 70 c.c.), was a colourless oil (46 g.), b. p. 128—133°/4 mm. (Found: C, 63·9; H, 11·2. $C_{11}H_{23}OCl$ requires C, 64·1; H, 11·2%).

Dibutylvinylcarbinol.—The chloro-compound (17 g.) was left at room temperature with potassium hydroxide (5·1 g.) in methyl alcohol (25 c.c.) for 3 hours; the mixture was then boiled for 5 hours and worked up in the same way as the benzyl compound. The unsaturated *carbinol* (7 g.) had b. p. 125°/34 mm. (Found: C, 77·9; H, 12·7. $C_{11}H_{22}O$ requires C, 77·7; H, 12·9%). It was unchanged after being heated with an equal weight of oxalic acid at 125—135° for 2 hours.

β-*Piperidinoethyldibutylcarbinol* was prepared from the chloro-carbinol (41 g.) and piperidine (36 c.c.) and obtained as a colourless oil (27·5 g.), b. p. 140—143°/5 mm. (Found: C, 75·7; H, 12·9. $C_{16}H_{33}ON$ requires C, 75·3; H, 13·0%). An attempt to prepare the *p*-nitrobenzoate gave a black tar.

γγ-*Diphenylallyl Chloride*.—Phenylmagnesium bromide (from magnesium, 24·3 g., and bromobenzene, 104·6 c.c.) was added to ethyl β-chloropropionate (68 g.) in ether; two layers were formed. On decomposition and distillation, two fractions were obtained: (a) 11 g., b. p. 108—110°/4 mm., 126—129°/14 mm.; (b) 27 g., b. p. 159—161°/4 mm. Fraction (b) was γγ-*diphenylallyl chloride* (Found: C, 78·7; H, 6·4; Cl, 15·0. $C_{15}H_{13}Cl$ requires C, 78·9; H, 6·0; Cl, 15·1%). A portion of it (9·1 g.) was introduced into phenylmagnesium bromide solution (magnesium, 3·1 g.; bromobenzene, 5·3 c.c.) and boiled for 2 hours. The isolated αα-diphenyl-β-benzylethylene boiled at 215°/12 mm. (compare Ziegler, Grabler, and Ulrich, *Ber.*, 1924, **57**, 1989; Schlenk and Bergmann, *Annalen*, 1928, **463**, 50) (Found: C, 92·9; H, 7·1. Calc. for $C_{21}H_{18}$: C, 93·3; H, 6·7%). Fraction (a), despite its constant b. p., was a mixture (Found: C, 72·8, 72·5; H, 7·5, 7·4; Cl, 9·9, 9·8. Calc. for C_9H_9OCl: C, 64·3; H, 5·4; Cl, 21·0%). When treated with phenylmagnesium bromide as fraction (b) was treated, it gave β-phenylpropiophenone, m. p. 72° (Found: C, 85·2; H, 7·3. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%) (compare Kohler, *Amer. Chem. J.*, 1909, **42**, 390).

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95. *Dipole Moment and Molecular Structure. Part XVI. Configuration of Ethylenic Compounds.*

By ERNST BERGMANN.

THE application of dipole moments to the determination of configuration is particularly useful in the case of rigid molecules, *e.g.*, benzene and ethylene derivatives; for the latter, only scanty data are available (Errera, *Physikal. Z.*, 1926, **27**, 764; 1928, **29**, 689; *J. Phys. Radium*, 1925, **6**, 390; Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446).

I. Ethylene compounds in this series contain substituents with axes of symmetry in the direction of their bonding. The following table records the dipole moments (Debye units) determined in solution.

Compound.	μ.	Compound.	μ.
*iso*Stilbene	0 [1]	αβ-Diphenyl-*p*-chlorostyryl bromide, m. p. 160°	2·61
Stilbene	0 [2]	αβ-Diphenyl-*p*-chlorostyryl bromide, m. p. 113°	1·57
pp'-Dinitrostilbene, m. p. 225°	0	αβ-Diphenylstyryl chloride	1·53
αβ-Dichlorostilbene, m. p. 144°	0	α-Bromostilbene, m. p. 31°	1·38
,, ,, m. p. 60°	2·60	,, ,, liquid	1·30
αβ-Dibromostilbene, m. p. 88°	2·53 [3]		
αβ-Dinitrostilbene, m. p. 186°	0		

[1] Wildschut, Thesis, Delft, 1932. [2] Smyth and Dornte, *J. Amer. Chem. Soc.*, 1931, **53**, 1296.
[3] For the higher-melting isomeride, which is obviously the *trans*-form, and for αβ-di-iodostilbene, no suitable solvent has been found.

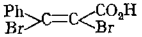
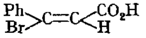
For the compounds containing two halogeno- or nitro-substituents, it is evident that a vanishing moment indicates a *trans*-, and a finite moment a *cis*-configuration. The lower-melting form of αβ-diphenyl-*p*-chlorostyryl bromide would appear to be a mixture or molecular compound of the *cis*- and the *trans*-isomeride. The same explanation applies to the β-phenyl-*p*-chloro- and -*p*-bromo-styryl bromides (Bergmann, Engel, and Meyer, *loc. cit.*). The tendency of substances of this group to form molecular compounds is shown by the fact that tolan gives a *molecular compound* (1 : 2) with *cis*-αβ-dibromo- or -dichloro-stilbene, and a *compound* (1 : 1) with *trans*-αβ-dibromostilbene (thermal analysis). No conclusion can be drawn as to the structure of the α-bromostilbenes from the dipole moments.

II. Dipole moments are not so readily applicable for the determination of configuration of "irregular" substituents, but in favourable cases it is possible to reach definite conclusions. Ethyl cinnamate and *allo*cinnamate have nearly the same moment, which is

Compound.	μ.	*Compound.*	μ.
Ethyl cinnamate	1·84	Methyl β-bromocinnamate (m. p. 134°) *	1·81
Ethyl *allo*cinnamate	1·77	(Methyl *p*-bromobenzoate	1·82)
Ethyl β-phenylcinnamate	1·98	Benzylideneacetophenone	2·92
Methyl α-phenylcinnamate	1·92	*p*-Bromobenzylideneacetophenone	2·47
(*o*-Phenylbenzonitrile	3·81)	Benzylidene-*p*-bromoacetophenone	2·93
Ethyl *p*-nitrocinnamate	3·50	*pp'*-Dibromobenzylideneacetophenone	2·03
Methyl *p*-nitro-α-phenylcinnamate	3·78	αβ-Dibromobenzylideneacetophenone (m. p. 113—114°)	3·17
(Ethyl *p*-nitrobenzoate	3·84)	β-Bromobenzylideneacetophenone	3·59
Methyl αβ-dibromocinnamate (m. p. 134°)*	1·89	α-Bromobenzylideneacetophenone	3·87
Ethyl αβ-dibromocinnamate (m. p. 134°) *	1·98	Ethyl α-bromocinnamate (m. p. 131°) *	2·25
Methyl αβ-dibromocinnamate (m. p. 100°)*	2·68	Ethyl α-bromocinnamate (m. p. 126°) *	2·80
Ethyl β-bromocinnamate (m. p. 159°) *	2·63		

* The m. p.'s are those of the corresponding acids.

not markedly affected by the introduction of phenyl groups into the α- or the β-position, and similarly for benzonitrile and its *o*-phenyl compound. Ethyl *p*-nitrocinnamate is undoubtedly the *trans*-compound, since its moment is smaller than that of the nitro-group and similar to that of ethyl *p*-nitrobenzoate. The same applies to ethyl *p*-nitro-α-phenyl-cinnamate.

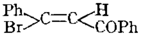
(I.)     (II.)

The ester of that αβ-dibromocinnamic acid in which the two bromine moments neutralise each other is expected to have the same moment as ethyl cinnamate; therefore, the acid, m. p. 100°, has formula (I), in agreement with the fact that the acid is easily cyclised to 2 : 3-dibromoindone (Pfeiffer and co-workers, *Annalen*, 1928, **467**, 158; *J. pr. Chem.*, **1929**, **121**, 85) (see also Stoermer and Heymann, *Ber.*, 1913, **46**, 1253; Stoermer and Kirchner, *Ber.*, 1920, **53**, 1290; Agyar, *Nature*, **1934**, **134**, 535). Also, Werner's rule ("Textbook of Stereochemistry," p. 214; Arends, *Ber.*, 1931, **64**, 1936) that *trans*- have a weaker absorption than the *cis*-isomerides is valid in the case of the αβ-dibromocinnamic acids but not in that of αβ-dichloro- and αβ-dibromo-stilbenes.

The ester of the acid (II) would be expected to have a moment similar to that of ethyl *p*-bromobenzoate, that of the *cis*-form being higher; therefore, the acid, m. p. 134°, corresponds to (II). These conclusions are contrary to the generally accepted views (see, *e.g.*, Auwers and Wolter, *Annalen*, 1932, **492**, 283) and will be discussed elsewhere.

Similar considerations apply to the derivatives of benzylideneacetophenone, the moment

of which is indistinguishable from that of benzophenone (compare ethyl benzoate and ethyl cinnamate). Comparison of benzylidene-*p*-bromo- with *pp'*-dibromobenzylidene-acetophenone (2·93 and 2·03) and of benzylidene- with *p*-bromobenzylidene-acetophenone (2·92 and 2·47) shows that the latter compounds contain the polar groups in the *trans*-position. In αβ-dibromobenzylideneacetophenone the bromine moments neutralise each

(III.)  (IV.)

other and are therefore in the *trans*-position (III). For similar reasons, in (IV) the polar groups must lie on the same side of the double bond.

Probably that form of α-bromobenzylideneacetophenone investigated corresponds configuratively to the α-bromocinnamic acid of m. p. 126° (moment of the ester 2·80); both have much higher moments than the non-brominated parent substances.

III. *In connexion with the above investigations, the dipole moments of some related* substances have been measured. The moments of ethyl *p*-nitro- and methyl *p*-bromo-β-

Compound.	μ.	Compound.	μ.
Ethyl β-phenylpropionate	1·75	Phenylchloroacetylene	1·21 [3]
Ethyl *p*-nitro-β-phenylpropionate	4·58	Ethyl *p*-phenylbenzoate	2·01 [4]
Methyl *p*-bromo-β-phenylpropionate	2·39	ω-Nitrostyrene	4·48
Tolan	0 [1]	ω-Chlorostyrene	1·40
Ethyl phenylpropiolate	2·19 [2]	ω-Bromostyrene	1·51
Ethyl *p*-nitrophenylpropiolate	3·54	ω-Ethoxystyrene	1·68

[1] Cf. Weissberger and Sängewald (*Z. physikal. Chem.*, 1933, *B*, **20**, 145) and the erroneous determination by Smyth and Dornte (*J. Amer. Chem. Soc.*, 1931, **53**, 1296). [2] Cf. the high value found by Otto (*ibid.*, 1934, **57**, 1263) and the data for phenylacetylene (Smyth and Dornte, *loc. cit.*; Bergmann and Tschudnovsky, *Z. physikal. Chem.*, 1932, *B*, **17**, 116). [3] Cf. Pflaum and Wenzke, *J. Amer. Chem. Soc.*, 1934, **56**, 1106. [4] Cf. Weissberger, *Z. physikal. Chem.*, 1933, *B*, **20**, 145.

phenylpropionate point definitely to a kind of *cis*-structure for these compounds, since their moments are higher than those of ethyl *p*-nitro- and ethyl β-bromo-cinnamate, respectively. Ramart-Lucas (Solvay lecture, 1931) assigned a " *cis*-structure " to β-phenylpropionic acid. The moment of ethyl *p*-nitrophenylpropiolate, which is almost identical with that of ethyl *trans*-*p*-nitrocinnamate, shows that the acetylene compound is straight.

Experimental.

Materials.—*iso*Stilbene (Schlenk and Bergmann, *Annalen*, 1928, **463**, 115) had b. p. 148—149°/17 mm. *pp'*-Dinitrostilbene (Walden and Kernbaum, *Ber.*, 1890, **23**, 1959) was recrystallised from glacial acetic acid, m. p. 280—285°. αβ-Diphenylstyryl chloride (Bergmann and Bondi, *Ber.*, 1931, **64**, 1467), m. p. 117°. *o*-Phenylbenzonitrile (Schlenk and Bergmann, *Annalen*, 1928, **464**, 34) had m. p. 41° (Pfeiffer *et al.*, *ibid.*, **467**, 174 describe it as an oil). Ethyl β-phenylcinnamate (Schlenk and Bergmann, *ibid.*, 1928, **463**, 237), b. p. 205°/16 mm. Ethyl *p*-nitrocinnamate (Drewsen, *ibid.*, 1882, **212**, 150), m. p. 141°, from alcohol. Methyl α-phenylcinnamate (Bergmann and Schreiber, *Ber.*, 1933, **66**, 44), m. p. 75°. Benzylideneacetophenone (Schlenk and Bergmann, *Annalen*, 1928, **463**, 234), m. p. 55°. *p*-Bromobenzylideneacetophenone (Weygand, *ibid.*, 1927, **459**, 118), from methyl alcohol, m. p. 120°; yield 65%. Benzylidene-*p*-bromoacetophenone (Bergmann and Hampson, J., 1935, 989), from light petroleum, m. p. 105°. *pp'*-Dibromobenzylideneacetophenone (Bergmann, Hoffmann, and Meyer, *J. pr. Chem.*, 1932, **135**, 252; cf. Blatt, *J. Amer. Chem. Soc.*, 1931, **53**, 1139), from toluene, m. p. 185—186°. Tolan (Schlenk and Bergmann, *Annalen*, 1928, **463**, 76), b. p. 158°/12 mm., from light petroleum, m. p. 60°. Ethyl phenylpropiolate, from the acid (Schlenk and Bergmann, *ibid.*, p. 82), had b. p. 137—138°/12 mm. Ethyl *p*-nitrophenylpropiolate, from the crude acid (Perkin and Bellenot, J., 1886, **49**, 441), had m. p. 126°. Phenylchloroacetylene (Truchat, *Ann. Chim.*, 1931, **16**, 309), b. p. 74°/15 mm. ω-Nitrostyrene (Thiele and Haeckel, *Annalen*, 1902, **325**, 7), from methyl alcohol, m. p. 60°. ω-Ethoxystyrene (Nef, *Annalen*, 1899, **308**, 26), b. p. 98—100°/13 mm. ω-Chlorostyrene (Erlenmeyer, *Ber.*, 1881, **14**, 1868; see Biltz, *Annalen*, 1879, **296**, 266), b. p. 89°/17 mm. Ethyl cinnamate (b. p. 263°), methyl *p*-bromobenzoate (m. p. 81°), ethyl *p*-nitrobenzoate (m. p. 57°), ethyl β-phenylpropionate (b. p. 242°), and ω-bromostyrene (b. p. 108°/20 mm.) were commercial samples.

αβ-Dichlorostilbenes. (*a*) By Blank's method (*Annalen*, 1888, **248**, 21), 30 g. of tolan on chlorination by 12 g. of the gas afforded first 0·8 g. (Found: C, 67·2; H, 4·3. Calc. for $C_{14}H_{10}Cl_2$: C, 67·5; H, 4·0%), m. p. 143—144°; and ether extraction of the residue of the mother-liquors gave a product which, after several recrystallisations from methyl alcohol, had m. p. 67—69°, and was a *molecular compound* (see below) (Found: Cl, 20·9. $2C_{14}H_{10}Cl_2,C_{14}H_{10}$ requires Cl, 21·0%).

(*b*) Tolan tetrachloride (24 g.; Redsko, *Ber.*, 1889, **22**, ref., 760) was heated with copper bronze (25 g.) (see Onufrowicz, *Ber.*, 1884, **17**, 835) under reduced pressure (20 mm.) in a Claisen flask. At 220° (bath temp.) a colourless liquid distilled over, which crystallised rapidly. The crude product was shaken for 12 hours with 100 c.c. of alcohol (which does not dissolve the higher-melting αβ-dichlorostilbene formed), the alcohol distilled off, and the residue triturated with ice-cold light petroleum. The substance, recrystallised from methyl alcohol, had m. p. 60°. When methyl-alcoholic solutions of this (2 mols.) and tolan (1 mol.) were mixed, characteristic crystals of the above double compound were obtained; m. p. and mixed m. p. 65—66°.

αβ-Dibromostilbenes. (*a*) The bromination product of tolan in ether (Limpricht and Schwanert, *Ber.*, 1871, **4**, 379) was extracted with hot alcohol after evaporation of the ether. The greater part of the higher-melting isomeride remained undissolved, and was recrystallised from propyl alcohol; m. p. 206—208°; yield, 70% (Found: C, 49·8; H, 3·2. Calc. for $C_{14}H_{10}Br_2$: C, 49·7; H, 3·0%). The alcoholic extract gave on cooling a further crop of the higher-melting compound; its mother-liquor gave on evaporation a residue, which was recrystallised several times from methyl alcohol. The long brittle needles, m. p. 77°, were a *molecular compound* (see below) (Found: C, 59·3; H, 3·7. $2C_{14}H_{10}Br_2,C_{14}H_{10}$ requires C, 59·0; H, 3·5%).

(*b*) 5 G. of the higher-melting compound were partly isomerised (see Limpricht and Schwanert, *loc. cit.*) by 18 hours' heating with 20 c.c. of water in a sealed tube at 180°. From the crystalline mass obtained, the lower-melting isomeride was extracted with cold alcohol; the solution was evaporated, and the residue triturated with ice-cold light petroleum, filtered off, and several times fractionated from the same solvent; m. p. 66—68° (yield, very small). With tolan in light petroleum (ratio 2 : 1), the substance gave the above double compound, m. p. 77°.

αβ-Di-iodostilbene. The product from tolan and iodine (Fischer, *Annalen*, 1882, **211**, 233) was triturated with cold chloroform, and the residue several times recrystallised from the same solvent; leaflets, m. p. 204° (decomp.) (yield, 10%) (Found: I, 58·6. Calc. for $C_{14}H_{10}I_2$: I, 59·0%).

αβ-Dinitrostilbene. The crystals prepared by Schmidt's method (*Ber.*, 1901, **34**, 621) were recrystallised six times from alcohol; yellowish prisms, m. p. 185—186°. The lower-melting iosmeride could not be detected.

αβ-Diphenyl-p-chlorostyryl bromides. Koelsch (*J. Amer. Chem. Soc.*, 1932, **54**, 2487) stated that apparently uniform preparations of certain triarylvinyl bromides gave, on treatment with magnesium and then with carbon dioxide, mixtures of stereoisomeric triarylacrylic acids. It is more likely that the ability of bromides to form mixed crystals or molecular compounds prevents final purification in these cases. αβ-Diphenyl-*p*-chlorostyrene (31 g.) in glacial acetic acid (100 c.c.) was treated with bromine (5·2 c.c.) in the same solvent (10 c.c.), and the resulting crystals were heated with benzene. Hydrogen bromide was vigorously evolved, and the clear solution obtained was evaporated, the residue washed with methyl alcohol, and recrystallised several times from propyl and amyl alcohol; yield, 14·5 g., m. p. 160°. The glacial acetic acid mother-liquor was poured into a large volume of water, extracted with ether, and the solution evaporated. Several recrystallisations of the remaining crop from alcohol and glacial acetic acid gave a substance, m. p. 112—113° (not sharp), which was proved by dipole-moment measurements to be a double compound of both the possible isomerides.

α-Bromostilbenes. (*a*) From stilbene dibromide (m. p. 239°), by the method of Wislicenus and Seeler (*Ber.*, 1895, **28**, 2693), an oil was finally obtained, but it could not be purified because distillation (b. p. 187—191°/17 mm.) caused partial isomerisation.

(*b*) The same procedure with stilbene dibromide (m. p. 110°; 7·5 g.) and potassium hydroxide (1·3 g.) gave the solid α-bromostilbene, which could be separated from the crude product by means of cold benzene. The benzene solution was evaporated in a vacuum desiccator, and the remaining crystals had m. p. 31°.

Ethyl allo*cinnamate.* Ethyl phenylpropiolate (15 g.) in alcohol (20 c.c.) was catalytically hydrogenated in presence of a palladium–barium sulphate catalyst (1·5 g.) at room temperature. The required amount of hydrogen was absorbed in about 3 hours; b. p. 131—134°/17 mm.; yield 11 g. (Found: C, 75·0; H, 7·0. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·8%).

Methyl p-*nitro-α-phenylcinnamate.* Prepared by recorded methods (Bakunin, *Gazzetta*, 1895,

25, I, 146, 175; 1901, 31, II, 83; see Sudborough and Lloyd, J., 1898, 73, 90), this formed prisms, m. p. 141—142°, from alcohol.

αβ-Dibromocinnamic acids. Phenylpropiolic acid (40 g.) was treated with bromine (44 g.) in ice-cold chloroform, the solvent evaporated, and the residue triturated with benzene and light petroleum (1 : 1) and recrystallised from benzene. The large colourless leaflets of the *trans*-isomeride (20 g., m. p. 134°) crystallised first, then the yellow prisms of the *cis*-acid (1·2 g., m. p. 98°). The addition of bromine is, therefore, largely a "*trans*-reaction." The methyl ester of the *cis*-acid (1·2 g.) was prepared by use of diazomethane (0·2 g.) in ether; yield, 1 g., b. p. 171—172°/18 mm. (Found : C, 37·7; H, 2·7. Calc. for $C_{10}H_8O_2Br_2$: C, 37·5; H, 2·5%). In the same way the *trans*-acid (5 g.) and diazomethane (1 g.) gave the corresponding methyl ester (4·1 g.), b. p. 167°/15 mm. On esterification with 3% alcoholic hydrochloric acid (boiling for 48 hours), no stereochemical rearrangement of the *trans*-acid occurred; the ester, b. p. 174°/12 mm., contained the bromine atoms in the *trans*-position.

β-Bromocinnamic acids. By the method of Sudborough and Thompson (J., 1903, 83, 1156), phenylpropiolic acid (22 g.) afforded ultimately 20 g. of the *trans*-acid (m. p. 132—134°) and 10·5 g. of the *cis*-acid (m. p. 159°), the preponderance of the former acid being contrary to recorded results. (Debromination of the β-bromocinnamic acids is accompanied by total configurational inversion, and is therefore not simply a substitution of hydrogen for the bromine atom, but more probably addition of hydrogen to the double bond, followed by elimination of hydrogen bromide; in the intermediate stage, the configurational rigidity of the molecules is lost and steric change can occur.) The higher-melting acid (5 g.) gave with diazomethane (1 g.) in ether the methyl ester (3·9 g.), m. p. 58°, from alcohol. The lower-melting acid was quantitatively esterified with 3% alcoholic hydrochloric acid; the *ester* had b. p. 171—172°/18 mm. (Found : C, 51·8; H, 4·5. $C_{11}H_{11}O_2Br$ requires C, 51·8; H, 4·3%). In both esterification reactions, no configurational change occurs (cf. Auwers and Schmellenkamp, *Ber.*, 1921, 54, 624; James, J., 1911, 99, 1626).

αβ-Dibromobenzylideneacetophenone. This was prepared according to Dufraisse (*Compt. rend.*, 1920, 171, 1062) from benzoylphenylacetylene (Nef, *Annalen*, 1899, 308, 267), and recrystallised from alcohol, and then from light petroleum; m. p. 113—114°. β-Bromobenzylideneacetophenone (Dufraisse, *loc. cit.*) was a yellow, thick oil, b. p. 219—220°/14 mm.; and the α-isomeride (Abell, J., 1912, 101, 1002) had b. p. 218—219°/14 mm., but could not be induced to crystallise.

α-Bromocinnamic acids. (*a*) Higher-melting acid. Phenylpropiolic acid was treated with a stream of gaseous hydrogen bromide (see J., 1903, 83, 1156), and the product purified through the barium salt; m. p. 130—131°. Esterification with 3% alcoholic hydrogen chloride (4 hours' boiling) afforded the ester, b. p. 169°/15 mm., in 75% yield.

(*b*) Lower-melting acid. αβ-Dibromo-β-phenylpropionic acid was treated with alcoholic potash solution (Sudborough and Thompson, *loc. cit.*); purification through the barium salt, and recrystallisation from benzene-light petroleum afforded the acid; m. p. 120°. The silver salt (10 g.) was heated with iodine-free ethyl iodide (9·3 g.) and a few c.c. of absolute ether in a sealed tube for 1 hour at 100°; the mass was extracted with ether, and the residue distilled in a vacuum; b. p. 156—157°/15 mm. (yield, 2 g.).

Methyl p-*bromo-β-phenylpropionate.* The acid (8 g.) (Glaser, *Annalen*, 1867, 143, 341; from methyl alcohol, m. p. 136°) was esterified with diazomethane (2 g.) in ether, affording the *ester* in quantitative yield; b. p. 154—155°/16 mm. (Found : C, 49·6; H, 4·8. $C_{10}H_{11}O_2Br$ requires C, 49·4; H, 4·5%).

Ethyl p-*phenylbenzoate.* 4-Acetyldiphenyl (*J. Amer. Chem. Soc.*, 1930, 52, 3718) (30 g.), potassium hydroxide (18 g.), potassium permanganate (96 g.), and water (1 l.) were boiled for 3 hours; the colourless liquid was immediately filtered and acidified, affording 17 g. of *p*-phenylbenzoic acid, m. p. 210°. The acid (30 g.) was boiled with thionyl chloride (120 g.) for 5 hours, the excess chloride distilled off, and the *acid chloride* recrystallised from light petroleum, forming clusters of needles, m. p. 112° (24 g.) [Found (method of Baubigny) : Cl, 16·6. $C_{13}H_9OCl$ requires Cl, 16·2%]. It (7·5 g.) was treated with alcohol (40 c.c.) at room temperature (24 hours), and the solution boiled, filtered, and cooled, the resulting leaflets being recrystallised from light petroleum; m. p. 45°.

Measurements.—In the following tables, c = molar fraction, $\overline{M}$ = average molecular weight of the solution, ζ = density, ϵ = dielectric constant, n = refractive index, P_1 (P_{E_1}) = total (electronic) polarisation of the solution, P (P_E) = the same for the solute, P_{A+O} = (atomic and) orientation polarisation, which is extrapolated graphically for infinite dilution. Most of the experiments were carried out in benzene as solvent. The dipole moment of *pp'*-dibromo-

benzylideneacetophenone was determined in dioxan, that of *pp'*-dinitrostilbene, m. p. 285°, in α-methylnaphthalene. The physical constants of dioxan were taken from the data of Williams (*J. Amer. Chem. Soc.*, 1930, **52**, 1831, 1838; see Bergmann and Schuetz, *Z. physikal. Chem.*, 1932, *B*, **19**, 395) and from unpublished work done in our laboratory. The data for α-methylnaphthalene are due to Bergmann and Schuetz (*loc. cit.*). The experiments were made partly in collaboration with Dr. W. Schuetz.

*iso*Stilbene; t = 17·6°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	78	0·8815	2·2888	2·2888	26·590	26·590	—	—	—
0·02039	80·080	0·8875	—	2·3081	—	27·397	—	66·16	—
0·03542	81·613	0·8919	2·3133	2·3223	27·860	27·993	62·44	66·20	—
0·05480	83·590	0·8977	2·3262	2·3400	28·546	28·751	62·27	66·02	—
0·06664	84·797	0·9011	2·3351	2·3504	28·980	29·209	62·46	65·90	—

$\mu = 0$.

pp'-Dinitrostilbene (m. p. 285°) in α-methylnaphthalene; t = 16·4°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	142	1·0240	2·7336	2·7336	50·787	50·787	—	—	—
0·00047	142·06	1·0241	2·7347	2·7345	50·824	50·820	131·05	121·68	—

$\mu \sim 0$.

αβ-Dichlorostilbene (m. p. 143—144°); t = 15·25°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	78	0·8843	2·2935	2·2935	26·575	26·575	—	—	—
0·00475	78·812	0·8880	2·2989	2·2983	26·816	26·807	77·28	75·36	—
0·01240	80·121	0·8941	2·3074	2·3066	27·199	27·188	76·93	75·97	—

$\mu = 0$.

αβ-Dichlorostilbene (m. p. 60°); t = 19·9°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	78	0·8788	2·2842	2·2842	26·606	26·606	—	—	→
0·00599	79·024	0·8829	2·3506	2·2898	27·786	26·911	223·74	77·55	146·19
0·00707	79·210	0·8836	2·306	2·2909	27·966	26·969	218·82	77·85	140·97
0·01423	80·434	0·8886	2·4422	2·2083	29·470	27·341	227·81	78·25	149·56
0·01634	80·794	0·8900	2·4669	2·3007	29·811	27·456	222·74	78·58	144·16

P^{∞}_{A+O} = 152·5. μ = 2·69.

αβ-Dibromostilbene (m. p. 68°); t = 19·9°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	78	0·8788	2·2842	2·2842	26·606	26·606	—	—	→
0·00548	79·425	0·8860	2·3415	2·2913	27·699	26·974	225·88	93·75	132·13

$P^{\infty}_{A+O} \sim$ 435. μ = 2·53.

αβ-Dinitrostilbene (m. p. 185—186°); t = 16·4°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	78	0·8829	2·2012	2·2912	26·583	26·583	—	—	—
0·00519	78·996	0·8873	2·2964	2·2068	26·863	26·869	80·57	81·65	—
0·00657	79·261	0·8884	2·2982	2·2983	26·948	26·949	82·08	82·27	—

$\mu = 0$.

αβ-Diphenyl-*p*-chlorostyryl bromide (m. p. 160°); t = 17·1°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	78	0·8821	2·2898	2·2898	26·587	26·587	—	—	→
0·00706	80·058	0·8919	2·3716	2·3025	28·163	27·173	249·73	109·59	140·14
0·00828	80·413	0·8936	2·3872	2·3046	28·454	27·273	252·10	109·45	142·65
0·00958	80·792	0·8954	2·4069	2·3073	28·805	27·385	258·09	109·88	148·28
0·01054	81·072	0·8968	2·4175	2·3089	29·009	27·461	256·39	109·54	146·85

P^{∞}_{A+O} (average) = 144·48. μ = 2·61.

αβ-Diphenyl-*p*-chlorostyryl bromide (m. p. 113°); t = 16·2°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	78	0·8831	2·2916	2·2916	26·581	26·581	—	—	→
0·00967	80·818	0·8963	2·3366	2·3102	27·791	27·409	151·69	112·19	39·50
0·01414	82·123	0·9024	2·3684	2·3188	28·506	27·789	162·67	111·96	50·71
0·01935	83·642	0·9095	2·3973	2·3287	29·221	28·227	162·99	111·60	51·39

P^{∞}_{A+O} = 52·3. μ = 1·57.

αβ-Diphenylstyryl chloride; t = 17·5°.

c.	$\bar{M}$.	ζ.	ϵ.	n^2.	P_{12}.	$P_{E_{12}}$.	P.	P_E.	P_{A+O}.
0	78	0·8816	2·2890	2·2890	26·589	26·589	—	—	→
0·01025	80·153	0·8879	2·3395	2·3059	27·864	27·378	151·07	103·62	47·45
0·02160	82·590	0·8949	2·3907	2·3235	29·291	28·251	151·73	103·56	48·17
0·02710	83·758	0·8983	2·4240	2·3324	30·011	28·675	152·91	103·57	49·34
0·02970	84·311	0·8999	2·4389	2·3385	30·370	28·905	153·91	104·57	49·34

P^{∞}_{A+O} = 49·5. μ = 1·53.

α-Bromostilbene (m. p. 31°); $t = 20{\cdot}85°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8777	2·2823	2·2823	26·612	26·612	—	—	→
0·01676	81·033	0·8947	2·3512	2·3069	28·125	27·484	116·95	78·67	38·28
0·02433	82·403	0·9024	2·3813	2·3170	28·791	27·859	116·18	77·89	38·29
0·03352	84·067	0·9117	2·4173	2·3300	29·584	28·322	115·29	77·63	37·66
0·04392	85·949	0·9223	2·4594	2·3391	30·498	28·759	115·09	75·51	39·58

$P^{\infty}_{A+O} = 40{\cdot}05$. $\mu = 1{\cdot}38$.

α-Bromostilbene, liquid; $t = 23{\cdot}05°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8751	2·2778	2·2778	26·625	26·625	—	—	→
0·00796	79·441	0·8841	2·3039	2·2891	27·224	27·008	101·92	74·67	27·25
0·01033	79·870	0·8867	2·3142	2·2928	27·438	27·125	105·32	75·03	30·29
0·01895	81·429	0·8965	2·3458	2·3049	28·128	27·533	105·96	74·54	31·42

$P^{\infty}_{A+O} = 35{\cdot}4$. $\mu = 1{\cdot}30$.

Ethyl cinnamate; $t = 20{\cdot}2°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8784	2·2836	2·2836	26·608	26·608	—	—	→
0·01747	79·712	0·8836	2·3656	2·2921	28·218	27·156	(118·76)	57·99	(60·77)
0·02745	80·690	0·8866	2·4324	2·2972	29·411	27·473	128·73	58·13	70·60
0·03615	81·542	0·8892	2·4798	2·3015	30·292	27·747	128·53	58·13	70·40
0·04083	82·001	0·8906	2·5095	2·3045	30·822	27·905	129·83	58·38	71·45

$P^{\infty}_{A+O} = 71{\cdot}3$. $\mu = 1{\cdot}84$.

Ethyl *allo*cinnamate; $t = 15{\cdot}4°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8841	2·2932	2·2932	26·576	26·576	—	—	→
0·01694	79·660	0·8899	2·3678	2·2958	28·032	27·004	112·55	51·86	60·69
0·02472	80·422	0·8925	2·3084	2·2974	28·648	27·203	110·42	51·97	58·45
0·03246	81·181	0·8951	2·4401	2·2981	29·415	27·390	114·06	51·67	62·39
0·03969	81·889	0·8976	2·4704	2·3000	30·002	27·582	112·92	51·94	60·98

$P^{\infty}_{A+O} = 67{\cdot}2$. $\mu = 1{\cdot}77$.

Ethyl β-phenylcinnamate; $t = 18{\cdot}7°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8802	2·2866	2·2866	26·599	26·599	—	—	→
0·01678	80·920	0·8887	2·3937	2·2967	28·882	27·478	162·65	79·00	79·67
0·02138	81·721	0·8911	2·4226	2·3060	29·500	27·816	162·27	83·50	79·29
0·02567	82·466	0·8933	2·4458	2·3100	30·023	28·135	159·99	86·44	77·01

$P^{\infty}_{A+O} = 83{\cdot}0$. $\mu = 1{\cdot}98$.

o-Phenylbenzonitrile; $t = 17{\cdot}7°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8814	2·2886	2·2886	26·592	26·592	—	—	→
0·00324	78·327	0·8825	2·3567	2·2919	27·630	26·704	350·39	61·48	288·91
0·00490	78·495	0·8831	2·3952	2·2924	28·216	26·763	357·81	61·59	296·22
0·00656	78·663	0·8837	2·4344	2·2936	28·795	26·821	362·43	61·50	300·93
0·00994	79·004	0·8848	2·5095	2·2963	29·880	26·941	358·32	61·72	296·60

$P^{\infty}_{A+O} = 308{\cdot}0$. $\mu = 3{\cdot}81$.

Ethyl *p*-nitrocinnamate; $t = 21{\cdot}3°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8771	2·2814	2·2814	26·615	26·615	—	—	→
0·00475	78·678	0·8787	2·3779	2·2855	28·149	26·828	323·01	71·32	251·69
0·01176	79·682	0·8836	2·5209	2·2920	30·337	27·146	316·44	71·71	244·73
0·01486	80·125	0·8853	2·5841	2·2950	31·276	27·289	313·65	71·95	241·70

$P^{\infty}_{A+O} = 256{\cdot}4$. $\mu = 3{\cdot}50$.

Methyl α-phenylcinnamate; $t = 18{\cdot}4°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8806	2·2872	2·2872	26·596	26·596	—	—	→
0·00723	79·157	0·8839	2·3308	2·2950	27·519	27·003	154·37	82·96	71·41
0·01622	80·597	0·8880	2·3903	2·3046	28·743	27·506	158·84	82·87	76·06
0·02038	81·261	0·8899	2·4120	2·3093	29·223	27·743	155·48	82·91	72·57
0·02224	81·558	0·8908	2·4240	2·3108	29·477	27·840	156·19	82·56	73·63

$P^{\infty}_{A+O} = 78{\cdot}4$. $\mu = 1{\cdot}92$.

Methyl *p*-nitro-α-phenylcinnamate; $t = 16{\cdot}8°$.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·8824	2·2904	2·2904	26·585	26·585	—	—	→
0·00315	78·646	0·8853	2·3569	2·2068	27·670	28·811	369·68	98·24	271·44
0·00397	78·814	0·8861	2·3779	2·2999	27·996	26·878	381·43	100·25	271·18
0·00466	78·955	0·8867	2·3938	2·3008	28·247	26·932	383·38	101·03	282·35
0·00620	79·272	0·8881	2·4025	2·3039	28·573	27·043	350·18	100·26	249·92

$P^{\infty}_{A+O} = 305{\cdot}0$. $\mu = 3{\cdot}78$.

Methyl $\alpha\beta$-dibromocinnamate (m. p. 134°); t = 21·4°.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{Et}.	P.	P_E.	P_{A+O}.
0	78	0·08771	2·2814	2·2814	26·615	26·615	—	—	→
0·01452	81·718	0·9023	2·3713	2·2905	28·413	27·242	150·39	69·77	80·62
0·01682	82·305	0·9062	2·3844	2·2921	28·677	27·340	149·21	69·72	79·49
0·02050	82·248	0·9126	2·4066	2·2942	29·117	27·492	148·66	69·38	79·28

P^{∞}_{A+O} = 82·1. μ = 1·98.

Methyl $\alpha\beta$-dibromocinnamate (m. p. 100°); t = 21·4°.

0	78	0·8770	2·2812	2·2812	26·616	26·616	—	—	→
0·00378	78·914	0·8847	2·3181	2·2836	27·227	26·728	(188·48)	56·18	(132·30)
0·00594	79·438	0·8891	2·3453	2·2851	27·674	26·793	204·82	56·45	148·37
0·00728	79·763	0·8919	2·3613	2·2859	27·914	26·833	204·88	56·36	148·52

P^{∞}_{A+O} = 150·6. μ = 2·68.

Methyl β-bromocinnamate (m. p. 159°); t = 21·6°.

0	78	0·8768	2·2807	2·2807	26·616	26·616	—	—	→
0·00903	79·599	0·8865	2·3726	2·2856	28·185	26·934	200·33	61·88	138·45
0·01371	80·426	0·8915	2·4163	2·2885	28·930	27·105	195·45	62·30	133·15
0·02016	81·569	0·8985	2·4874	2·2927	30·091	27·338	198·96	62·44	136·52
0·02649	82·689	0·9053	2·5482	2·2971	31·091	27·569	195·52	62·61	132·91

P^{∞}_{A+O} = 144·7. μ = 2·63.

Ethyl β-bromocinnamate (m. p. 134°); t = 19·2°.

0	78	0·8796	2·2856	2·2856	26·601	26·601	—	—	→
0·01247	80·032	0·8938	2·3455	2·2914	27·725	26·945	116·78	54·22	62·56
0·01460	80·380	0·8962	2·3591	2·2929	27·963	27·012	119·94	54·81	65·13
0·01972	81·214	0·9020	2·3849	2·2955	28·435	27·154	119·65	54·66	64·99
0·02660	82·336	0·9099	2·4162	2·2990	29·019	27·343	117·51	54·51	63·00

P^{∞}_{A+O} = 69·2. μ = 1·81.

Methyl p-bromobenzoate; t = 14·0°.

0	78	0·8857	2·2962	2·2962	26·569	26·569	—	—	→
0·01614	80·211	0·9036	2·3798	2·3015	27·965	26·858	113·08	44·47	68·61
0·02057	80·818	0·9085	2·4006	2·3029	28·313	26·963	111·34	44·37	66·97
0·02676	81·666	0·9154	2·4320	2·3048	28·827	27·042	110·94	44·23	66·71
0·03446	82·721	0·9239	2·4714	2·3074	29·464	27·177	110·57	44·20	66·37

P^{∞}_{A+O} = 70·9. μ = 1·82.

Benzylideneacetophenone; t = 19·8°.

0	78	0·8789	2·2844	2·2844	26·606	26·606	—	—	→
0·00710	78·924	0·8823	2·3813	2·2952	28·202	26·976	251·31	78·69	172·62
0·01176	79·528	0·8845	2·4492	2·3033	29·285	27·229	254·56	79·67	174·89
0·01614	80·099	0·8867	2·5155	2·3114	30·319	27·477	256·62	80·59	176·03

P^{∞}_{A+O} = 179·4. μ = 2·92.

pp'-Dibromobenzylideneacetophenone, in dioxan; t = 17·1°.

0	88	1·0343	2·4187	2·4187	27·318	27·318	—	—	→
0·00493	89·372	1·0425	2·4582	2·4370	28·040	27·764	173·60	90·43	83·17
0·00683	89·800	1·0457	2·4715	2·4460	28·293	27·961	169·92	90·13	79·79

P^{∞}_{A+O} = 88·0. μ = 2·03.

p-Bromobenzylideneacetophenone; t = 22·15°.

0	78	0·8761	2·2796	2·2796	26·619	26·619	—	—	→
0·00932	79·949	0·8882	2·3715	2·2993	28·239	27·201	200·36	89·03	111·33
0·01238	80·587	0·8922	2·4104	2·3044	28·885	27·373	209·65	87·47	122·18
0·01513	81·162	0·8958	2·4334	2·3111	29·294	27·554	203·43	88·43	115·00
0·01838	81·841	0·9000	2·4715	2·3189	29·926	27·770	206·54	89·23	117·31

P^{∞}_{A+O} = 127·7. μ = 2·47.

Benzylidene-p-bromoacetophenone; t = 18·2°.

0	78	0·8808	2·2876	2·2876	26·594	26·594	—	—	→
0·00998	80·085	0·8927	2·4319	2·3079	28·984	27·236	266·14	90·94	175·20
0·01189	80·485	0·8950	2·4603	2·3118	29·442	27·358	266·13	90·83	175·30
0·01525	81·187	0·8990	2·5082	2·3182	30·212	27·568	265·88	90·42	173·46
0·01926	82·025	0·9038	2·5648	2·3259	31·110	27·816	261·09	90·01	171·08

P^{∞}_{A+O} = 182·0. μ = 2·93.

$\alpha\beta$-Dibromobenzylideneacetophenone (m. p. 113—114°); t = 21·6°.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_1^*.	P_{E_1}.	P.	P_E.	P_{A+O}.
0	78	0·8768	2·2807	2·2807	26·616	26·616	—	—	→
0·00586	79·678	0·8885	2·3704	2·2886	28·122	26·948	283·83	83·25	200·58
0·00884	80·547	0·8945	2·4264	2·2993	28·878	27·125	282·40	84·19	198·21
0·01201	81·458	0·9009	2·4701	2·2980	29·373	27·306	286·50	84·11	202·39
0·01524	82·388	0·9074	2·5204	2·3032	30·539	27·498	284·10	84·52	199·58

P^{∞}_{A+O} = 210·0. μ = 3·17.

β-Bromobenzylideneacetophenone; t = 20·9°.

0	78	0·8776	2·2822	2·2822	26·612	26·612	—	—	→
0·00511	79·068	0·8842	2·3849	2·2900	28·244	26·891	346·10	81·07	265·03
0·00869	79·816	0·8888	2·4556	2·2957	29·339	27·089	240·42	81·45	258·97
0·01222	80·553	0·8933	2·5223	2·3014	30·356	27·284	333·00	81·56	251·44
0·01629	81·404	0·8985	2·6058	2·3074	31·588	27·499	332·12	81·07	251·05

P^{∞}_{A+O} = 271·2. μ = 3·59.

α-Bromobenzylideneacetophenone; t = 20·05°.

0	78	0·8786	2·2839	2·2839	26·608	26·608	—	—	→
0·00497	79·040	0·8851	2·3989	2·2913	28·399	26·871	386·74	79·65	307·09
0·00855	79·788	0·8898	2·4799	2·2970	29·621	27·065	378·85	80·09	298·76
0·01153	80·409	0·8937	2·5498	2·3020	30·647	27·230	377·11	80·62	296·49
0·01514	81·164	0·8985	2·6303	2·3082	31·807	27·431	370·01	80·98	289·03

P^{∞}_{A+O} = 316·1. μ = 3·87.

Ethyl α-bromocinnamate (m. p. 131°); t = 21·6°.

0	78	0·8768	2·2807	2·2807	26·616	26·616	—	—	→
0·01371	80·427	0·8907	2·3905	2·2907	28·598	29·163	171·13	66·48	104·65
0·02161	81·826	0·8987	2·4522	2·2970	29·697	27·481	169·16	66·63	102·53
0·03022	83·349	0·9075	2·5228	2·3042	30·924	27·831	169·18	66·82	102·36
0·03574	84·326	0·9131	2·5700	—	31·727	—	169·63	(66·65)	102·98

P^{∞}_{A+O} = 105·6. μ = 2·25.

Ethyl α-bromocinnamate (m. p. 126°); t = 19·4°.

0	78	0·8794	2·2852	2·2852	26·603	26·603	—	—	→
0·00418	78·741	0·8836	2·3331	2·2874	27·416	26·759	220·92	63·95	156·97
0·00466	78·825	0·8841	2·3400	2·2877	27·528	26·778	225·22	64·15	161·07
0·00710	79·257	0·8866	2·3592	2·2889	27·874	26·866	205·58	63·63	141·95
0·01090	79·940	0·8905	2·4010	2·2912	28·579	27·013	206·92	64·05	142·87

P^{∞}_{A+O} = 165·6. μ = 2·80.

Ethyl p-nitrobenzoate; t = 13·1°.

0	78	0·8868	2·2980	2·2980	26·562	26·562	—	—	→
0·00424	78·497	0·8899	2·3030	2·2988	27·971	25·650	358·46	47·32	311·14
0·00769	78·899	0·8924	2·4695	2·2998	29·068	26·726	352·56	47·86	304·70
0·01271	79·487	0·8961	2·5782	2·3011	30·577	26·833	342·60	47·91	294·69
0·01770	80·071	0·8997	2·6863	2·3021	32·023	26·934	335·15	47·61	287·54

P^{∞}_{A+O} = 318·0. μ = 3·84.

Ethyl β-phenylpropionate; t = 21·15°.

0	78	0·8773	2·2817	2·2817	26·614	26·614	—	—	→
0·02437	80·437	0·8837	2·3796	2·2787	28·673	27·203	111·08	50·75	60·33
0·03042	81·042	0·8853	2·4082	2·2782	29·243	27·350	113·02	50·80	62·22
0·03684	81·684	0·8870	2·4339	2·2777	29·782	27·507	112·59	50·84	61·75
0·04891	82·891	0·8902	2·4893	2·2767	30·891	27·799	114·05	50·83	63·22

P^{∞}_{A+O} = 64·57. μ = 1·75.

Ethyl p-nitro-β-phenylpropionate; t = 20·0°.

0	78	0·8787	2·2840	2·2840	26·607	26·607	—	—	→
0·00672	78·974	0·8827	2·4912	2·2851	29·704	26·829	487·69	59·65	428·04
0·00873	79·265	0·8840	2·5509	2·2856	30·556	26·898	479·19	59·91	419·28
0·01055	79·330	0·8851	2·6141	2·2859	31·431	26·958	483·91	59·90	424·01
0·01367	79·983	0·8871	2·7075	2·2867	32·705	27·064	472·57	60·07	412·50

P^{∞}_{A+O} = 442·8. μ = 4·58.

Methyl p-bromo-β-phenylpropionate; t = 19·8°.

0	78	0·8789	2·2844	2·2844	26·605	26·605	—	—	→
0·01147	79·893	0·8890	2·3585	2·2895	28·011	26·964	177·45	57·89	119·56
0·01470	80·425	0·8918	2·4100	2·2870	28·833	27·073	176·16	58·42	117·74
0·01994	81·290	0·8965	2·4303	2·2874	20·276	27·229	(160·55)	57·92	(102·63)
0·02521	82·160	0·9011	2·4974	2·2890	30·358	27·402	175·47	58·22	117·25

P^{∞}_{A+O} = 120·25. μ = 2·39.

c.	$\overline{M}$.	ζ.	ϵ.	n^2.	P_t.	P_{E_1}.	*P*.	P_E.	P_{A+O}.
				Tolan; *t* = 18·4°.					
0	78	0·8805	2·2872	2·2872	26·596	26·596	—	—	—
0·00249	78·249	0·8812	—	2·2901	—	26·703	—	69·46	—
0·00497	78·497	0·8819	—	2·2932	—	26·813	—	70·09	—
0·00744	78·744	0·8825	—	2·2963	—	26·923	—	70·46	—
0·02621	80·621	0·8875	2·3139	—	27·667	—	67·45 }		
0·3831	81·831	0·8907	2·3248	—	28·142	—	66·94 }	(70·00)	—
0·04728	82·728	0·8931	2·3344	—	28·517	—	67·21 }		
				μ = 0.					
				Ethyl *p*-nitrophenylpropiolate; *t* = 21·8°.					
0	78	0·8765	2·2803	2·2803	26·618	26·618	—	—	→
0·00634	78·894	0·8809	2·3993	2·2853	28·485	26·860	321·03	04·82	256·21
0·00847	79·194	0·8821	2·4397	2·2869	29·113	26·951	321·29	66·01	255·28
0·01194	79·684	0·8848	2·5058	2·2895	30·096	27·073	317·89	64·70	253·19
0·01628	80·296	0·8878	2·5865	2·2921	31·284	27·226	313·21	64·00	249·21
				P^{∞}_{A+O} = 262·0. μ = 3·54.					
				Ethyl phenylpropiolate; *t* = 20·5°.					
0	78	0·8781	2·2830	2·2830	26·611	26·611	—	—	→
0·01118	79·073	0·8817	2·3416	2·2868	27·714	26·922	125·31	54·46	70·85
0·01915	79·839	0·8842	2·4083	2·2900	28·844	27·150	143·23	54·78	88·45
0·02701	80·593	0·8868	2·4694	2·2933	29·879	27·378	147·64	55·01	92·63
0·03580	81·442	0·8896	2·5361	2·2971	31·002	27·634	149·08	55·14	93·94
				P^{∞}_{A+O} = 100·8. μ = 2·19.					
				Phenylchloroacetylene; *t* = 18·8°.					
0	78	0·8800	2·2864	2·2864	26·600	26·600	—	—	→
0·02600	79·521	0·8890	2·3462	2·2954	27·706	26·976	69·12	41·07	28·05
0·02800	79·638	0·8897	2·3554	2·2963	27·854	27·008	71·41	41·16	30·25
0·04544	80·658	0·8958	2·3887	2·3026	28·492	27·260	68·23	41·12	27·11
				P^{∞}_{A+O} = 31·0. μ = 1·21.					
				Ethyl *p*-phenylbenzoate; *t* = 14·6°.					
0	78	0·8850	2·2949	2·2949	26·573	26·573	—	—	→
0·00915	79·354	0·8906	2·3569	2·3032	27·750	26·984	155·32	71·61	83·71
0·01411	80·088	0·8936	2·3904	2·3075	28·383	27·204	154·91	71·36	83·55
0·01719	80·544	0·8955	2·4110	2·3104	28·771	27·343	154·48	71·37	83·11
0·01904	80·817	0·8966	2·4219	2·3120	28·984	27·425	153·26	71·36	81·90
				P^{∞}_{A+O} = 86·8. μ = 2·01.					
				ω-Nitrostyrene; *t* = 17·2°.					
0	78	0·8819	2·2896	2·2896	26·588	26·588	—	—	—
0·00528	81·748	0·8837	2·4439	2·2940	30·057	27·877	683·93	270·79	413·14
0·00750	83·327	0·8845	2·5105	2·2995	31·548	28·414	687·76	275·70	412·06
0·00890	84·317	0·8849	2·5542	2·2962	32·517	28·752	692·96	269·83	423·13
0·01191	86·460	0·8860	2·6461	2·2991	34·555	29·489	695·30	270·13	425·17
				P^{∞}_{A+O} = 427·0. μ = 4·48.					
				ω-Chlorostyrene; *t* = 18·8°.					
0	78	0·8800	2·2864	2·2864	26·600	26·600	—	—	—
0·02641	79·598	0·8883	2·3683	2·2962	28·069	27·037	82·23	43·14	39·09
0·03133	79·895	0·8897	2·3841	2·2982	28·351	27·123	82·50	43·28	29·22
0·03842	80·324	0·8918	2·4042	2·3007	28·717	27·242	82·71	43·32	39·39
0·04393	80·658	0·8929	2·4210	2·3030	29·036	27·355	82·06	43·79	38·27
				P^{∞}_{A+O} = 41·1. μ = 1·40.					
				ω-Bromostyrene; *t* = 18·0°.					
0	78	0·8810	2·2880	2·2880	26·594	26·594	—	—	—
0·02114	80·169	0·8961	2·3673	2·2993	28·009	27·036	93·58	47·55	46·03
0·02673	80·807	0·9001	2·3911	2·3024	28·440	27·175	95·68	48·35	47·33
0·03970	82·169	0·9094	2·4377	2·3010	29·273	27·464	94·09	48·52	45·57
0·05267	83·530	0·9187	2·4877	2·3171	30·142	27·740	93·97	48·37	45·60
				P^{∞}_{A+O} = 48·0. μ = 1·51.					
				ω-Ethoxystyrene; *t* = 18·3°.					
0	78	0·8807	2·2874	2·2874	26·596	26·596	—	—	—
0·02497	79·748	0·8896	2·3984	2·2965	27·501	27·051	102·91	44·83	58·08
0·03191	80·234	0·8921	2·9284	2·2986	29·110	27·170	102·27	44·60	57·67
0·03810	80·667	0·8943	2·4565	2·3007	29·479	27·281	102·30	44·59	57·71
0·04329	81·031	0·8962	2·4785	2·3028	29·851	27·378	101·81	44·66	57·15
				P^{∞}_{A+O} = 59·7. μ = 1·68.					

THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, March 6th*, 1935.]

96. *Synthetical Experiments with Benzhydrylsodium.*

By Ernst Bergmann.

The alkali-organic compounds have been used for many syntheses by Schlenk and his co-workers, but a systematic study of their applicability for preparative purposes has never been made. The present paper gives a list of experiments made with benzhydrylsodium, which is easily accessible from benzhydryl methyl ether and sodium (Ziegler and Thielmann, *Ber.*, 1923, **56**, 1740; Schlenk and Bergmann, *Annalen*, 1928, **464**, 18). The work parallels in some respects the extensive synthetical studies of Schlenk and Ochs (*Ber.*, 1916, **49**, 608) with triphenylmethylsodium and of Bergmann and Ukai (*Ber.*, **1933**, **66**, 54) with phenylstyrylmethylsodium. Benzhydrylsodium was chosen for the present experiments, not only because of its easy availability, but also since it does not incline so much to enolising reactions with carbonyl compounds as triphenylmethylsodium (see, *e.g.*, Schlenk, Hillemann, and Rodloff, *Annalen*, 1931, **487**, 135, for the reaction with ethyl diphenylacetate, and Schlenk and Bergmann, *Annalen*, 1930, **479**, 74, for the interaction with benzylacetone).

The reaction between benzhydrylsodium and aromatic ketones and thio-ketones has been studied systematically by Bergmann and Wagenberg (*Ber.*, 1930, **63**, 2585). They also reported some experiments with Δ^{α}-unsaturated ketones which led to addition at the carbon double bond. These results seemed worthy of extension; the following list includes the reactions with many compounds of the type mentioned; the table, which is self-explanatory, shows that *usually* benzhydrylsodium undergoes 1 : 4-addition to Δ^{α}-unsaturated carbonyl compounds. In view of this fact it is remarkable that ethyl phenylpropiolate reacts like a saturated ester; it gives a carbinol as with phenylmagnesium bromide (Hess and Weltzien, *Ber.*, 1921, **54**, 2511); the structure of the product follows from the fact that it is attacked by acetyl chloride. If it had the alternative formula

$$CHPh_2{\cdot}CPh{:}CH{\cdot}CO{\cdot}CHPh_2,$$

one molecule of benzhydrylsodium having reacted with the ester group, and another added to the triple bond, the product should be stable towards acetyl chloride. The behaviour of the Δ^{α}-unsaturated carbonyl compounds is all the more remarkable since phenyl-lithium reacts with benzylideneacetophenone as with any saturated ketone (Lüttringhaus, *Ber.*, **1934**, **67**, 1602).

The table shows that benzhydrylsodium reacts with enolisable esters to a certain extent in the normal way; some of it, however, is converted into diphenylmethane by the enolic form. Acyl chlorides of the corresponding type do not give condensation products, but react exclusively in their enolic form. Even with ethyl α-bromopropionate, normal condensation occurs, although it should incline largely to enolisation (compare the enolisation of bromoacetones : Hughes, Watson, and Yates, J., 1931, 3318; Watson and Yates, J., 1932, 1207). Only with ethyl fluorene-9-carboxylate did the enolic reaction prevail.

The reactions with benzhydrylsodium lead to rather highly phenylated substances. It seemed interesting to know whether very high phenylation of this type gives stable products or not. Here the experiment with β-benzpinacolin is instructive. The condensation product decomposes spontaneously according to the scheme :

$$CPh_3{\cdot}COPh + CHPh_2Na \longrightarrow CPh_3{\cdot}CPh(OH){\cdot}CHPh_2 \longrightarrow CHPh_3 + Ph{\cdot}CO{\cdot}CHPh_2$$

This reaction recalls similar observations of Kohler, Richtmyer, and Hester (*J. Amer. Chem. Soc.*, **1931**, **53**, 205) and Bergmann and Wolff (*ibid.*, **1932**, **54**, 1644).

Some of the experiments described herein were carried out at the Berlin University in collaboration with Dr. Alfred von Christiani.

Experimental.

For each experiment, 5 g. of benzhydryl methyl ether were split with sodium in about 200 c.c. of ether (2 days' shaking); the solution was decanted from the excess of sodium in a nitrogen atmosphere (Schlenk tube). Where any other quantity of the ether was used, it is noted in parentheses after the figure giving the amount of the reagent.

Reagent.	Wt., g.	Product.	Wt., g.	M. p.	B. p./mm.	Found, %. C.	Found, %. H.	Calc., %. C.	Calc., %. H.	Remarks.
β-Phenylethyl chloride	2·8	$CH_2Ph·CH_2·CHPh_2$	3·5	47°	225°/21	92·8	7·5	92·6	7·4	Needles, from MeOH [1]
α-Phenylethyl chloride	2·8	$CHPhMe·CHPh_2$	2·3	76	220/16	—	—	—	—	From MeOH [2]
Chlorodimethyl ether	2	$OMe·CH_2·CHPh_2$	4·5	—	198/19	85·0	7·6	84·9	7·5	
Formaldehyde	1	$OH·CH_2·CHPh_2$	2·7	59—60	—	84·6	7·3	84·8	7·1	From light petroleum
Benzaldehyde	4·8 (9)	$OH·CHPh·CHPh_2$	9	88—89	234/16	—	—	—	—	Needles, from EtOH or C_6H_6 [3]
Acetone	2·6 (9)	CH_2Ph_2	7·5	—	—	—	—	—	—	
Dibenzyl ketone	4·2	CH_2Ph_2	3·2	—	—	—	—	—	—	
Benzil	4·8 (9)	{Tetraphenylethane {Benzoin	— —	— —	209 135	—	—	—	—	Transfer of the metal from the alkali-organic compound to benzil
β-Benzpinacolin	6·2	{$Ph·CO·CHPh_2$ {$CHPh_2$	— —	— —	135 92	—	—	—	—	
Benzoin ethyl ether	4	CHPh·OEt $CPh(OH)·CHPh_2$	4	140	—	85·3	7·0	85·3	6·8	Rhombic crystals, from EtOH
Benzylideneacetophenone oxide	4·5	Ph·CH—CH·CPh·OH (—O—) $CHPh_2$	4·5	179—180	—	85·9	6·2	85·7	6·1	Needles, from PrᵅOH
p-Chlorobenzophenone	6·7 (7)	$C_6H_4Cl·CPh·OH$ $CHPh_2$	6·3	176—178	—	81·1	5·7	81·3	5·5	From PrᵅOH. *Dehydration with boiling AcCl gives* p-chlorotetraphenylethylene, needles, m. p. 166—167°, from PrᵅOH [4]
pp'-Dichlorobenzophenone	5	$(C_6H_4Cl)_2C(OH)·CHPh_2$	7·3	183—184	—	74·7	5·1	74·5	4·8	Needles, from light petroleum [5]
pp'-Dibromobenzophenone	6	$(C_6H_4Br)_2C(OH)·CHPh_2$	5·8	197	—	—	—	—	—	Needles, from PrᵅOH. Dehydration as above gives pp'-dibromotetraphenylethylene, needles, m. p. 205°, from light petroleum [6]
p-Methoxybenzophenone	4·5	$OMe·C_6H_4·CPh·OH$ $CHPh_2$	2	—	—	85·5	6·5	85·2	6·4	From PrᵅOH. p-Methoxytetraphenylethylene forms needles, m. p. 131—132° [7]
Benzylideneacetone	2	(CH_2Ph_2 and) $CHPh·CH_2·COMe$ $CHPh_2$	1	137	—	88·2	6·9	87·9	7·0	Needles, from PrᵅOH
Benzylideneacetophenone	4·5	$CHPh·CH_2·COPh$ $CHPh_2$	7·3	182—184	—	—	—	—	—	Needles from AcOH. No reaction with Br
p-Methoxybenzylidene acetophenone	4·8	$OMe·C_6H_4·CH·CH_2·COPh$ $CHPh_2$	6·8	146—148	—	85·5	6·6	85·7	6·4	From PrᵅOH; stable towards Br
Cinnamylideneacetophenone	8 (10)	$CHPh:CH·CH·CH_2·COPh$ $CHPh_2$	6·7	151—152	—	89·6	6·5	89·6	6·5	Needles, from AcOH or PrᵅOH; adds Br; stable against boiling AcCl
Benzophenonephenylmethylhydrazone	5·8	$Ph_2C·NH·NPhMe$ [and some $(CHPh_2)_2$] $CHPh_2$	4·5	149—151	—	87·7 N 6·2	6·5	87·2 N 6·2	6·6	Stout yellowish prisms, from C_6H_6 [8]
Benzyl benzoate	4·3	$Ph·CO·CHPh_2$	2·1	135	—	—	—	—	—	
Benzonitrile	2·3	$Ph·CO·CHPh_2$	4·1	135	—	—	—	—	—	
Ethyl o-methoxybenzoate	3·3	$OMe·C_6H_4·CO·CHPh_2$	2·3	86—87	—	83·6	5·9	83·4	6·0	Needles, from MeOH
Methyl o-fluorobenzoate	3·5	$C_6H_4F·CO·CHPh_2$	—	84—85	—	82·7	5·2	82·7	5·2	Diamond-shaped prisms, from light petroleum
Ethyl phenylpropiolate	3·5	$CPh:C·C(CHPh_2)_2·OH$	1·8	178—179	—	90·4	6·1	90·5	6·0	Lancet-shaped crystals, from amyl alcohol; adds 1 mol. Br
Ethyl fluorene-9-carboxylate	5·4	CH_2Ph_2	—	—	—	—	—	—	—	
Acetyl chloride	3·5 (9)	"	—	—	—	—	—	—	—	
Phenylacetyl chloride	7 (9)	"	—	—	—	—	—	—	—	
Ethyl α-bromopropionate	4·1	$CHPh_2·CHMe$ $CO·CHPh_2$ and	—	130—131	—	89·2	6·7	89·2	6·7	Needles, from PrᵅOH or petroleum
		(after hydrolysis) $CHPh_2·CHMe·CO_2H$	—	160—161	—	80·0	6·7	80·0	6·7	Leaflets, from 25% AcOH
Ethyl isobutyrate	2·4	(CH_2Ph_2 and) $CHMe_2·CO·CHPh_2$	1·5	75—76	—	85·7	7·6	85·4	7·6	Needles, from light petroleum
Ethyl α-benzylpropionate	3·8	(CH_2Ph_2 and) $CH_2Ph·CHMe$ $CO·CHPh_2$	1·8	—	250—252/16	88·0	7·1	87·9	7·1	
Ethyl dibenzylacetate	5·4	(CH_2Ph_2 and) $(CH_2Ph)_2CH$ $CO·CHPh_2$	2·2	107—108	—	89·2	6·7	89·2	6·7	Prismatic plates, from MeOH
Methyl cinnamate	4	$CHPh_2·CHPh$ $CH_2·CO_2Me$	—	126—127	—	83·7	7·0	83·6	6·7	Prisms, from MeOH or petroleum

[1] Ziegler, Grabbe, and Ullrich, *Ber.*, 1924, **57**, 1983.
[2] Schlenk and Bergmann, *Annalen*, 1928, **465**, 45.
[3] Gardeur, *Chem. Zentr.*, 1897, II, 661.
[4] Found: C, 85·1; H, 5·4. Calc. for $C_{26}H_{19}Cl$: C, 85·2; H, 5·2%. Compare Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2954; Norris and Tibbett, *J. Amer. Chem. Soc.*, 1921, **42**, 2091.
[5] Boiling acetyl chloride gives an anomalous product, m. p. 185—186° (from propyl alcohol), which has the composition $C_{26}H_{20}O_2Cl_2$ of a peroxide of the above carbinol.
[6] Found: C, 64·0; H, 3·7. Calc. for $C_{26}H_{18}Br_2$: C, 64·1; H, 4·1%.
[7] Found: C, 89·4; H, 6·2. Calc. for $C_{27}H_{22}O$: C, 89·4; H, 6·1%.
[8] For similar reactions, see Bergmann and Rosenthal, *J. pr. Chem.*, 1932, **135**, 267.

For other reactions of benzhydryl sodium, see Schlenk and Bergmann, *Annalen*, 1928, **464**, 1; 1930, **479**, 72; Bergmann and Weiss, *Ber.*, 1931, **64**, 1488.

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97. *The Veratrine Alkaloids. Part III. The Preparation of Cevanthrol, and the X-Ray Crystallographic Examination of Cevanthrol and Cevanthridine.*

By B. K. Blount and (Miss) D. Crowfoot.

The selenium dehydrogenation of cevine to a crystalline base $C_{23}H_{25}N$ (cevanthridine) was described in Part II (J., 1935, 124). By modifying the method of isolation, we have now obtained a second dehydrogenation product, $C_{17}H_{16}O$, which we have named *cevanthrol*, in just under 5% yield. Its oxygen atom is phenolic, since it dissolves in hot alkali and forms an *acetyl* derivative. The related hydrocarbon is therefore $C_{17}H_{16}$, which corresponds to a substituted phenanthrene, $C_{14}H_{10} + C_3H_6$.

In order to gain an insight into the structure of this substance and of cevanthridine we have made a preliminary *X*-ray examination of crystals of both of them. Table I gives the results obtained together with the approximate orientation of the optic axes in the crystals. The cell dimensions are correct to about 2%.

TABLE I.

Substance.	*a*.	*b*.	*c*.	—	Space group.	No. of mols. in unit cell.	No. in asymmetric unit.	Density calc.
Cevanthrol	16·7	7·0	23·8	107°	$P2_1/a$	8	2	1·17
	α	β	γ					
Cevanthridine	6·8	15·55	17·35	90°	$P2_1/a$?	4	1	1·13
	β	α	γ					

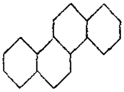
The crystal unit cell of cevanthrol contains eight molecules, twice as many as that required by the symmetry, and it is therefore impossible to determine with certainty their orientation in the unit cell. But the very marked weakening of the odd orders of the *c* plane indicates the presence of a double layer of molecules placed lengthwise along *c* (γ) such as is found in the fatty acids and alcohols. From this we may deduce approximately the orientations and dimensions of the molecules as length probably about 12 Å. along *c*/2 (γ), width 7 Å. along *b* (β), and thickness 4 Å. in the *a* plane, *a* sin β/4 (α). These dimensions agree closely with those found for other alkylphenanthrene derivatives in which the 9- and 10-positions are left unsubstituted (Bernal and Crowfoot, J., 1935, 93). Further, it is almost certain that the double layer is caused by the association of molecules together by bonds between the hydroxyl groups (Bernal and Megaw, *Proc. Roy. Soc.*, 1935, **151**, 384) such as occurs, for example, in the sterols (Bernal, *Nature*, 1932, **129**, 277) and in the more completely investigated structure of resorcinol (Robertson, *Nature*, 1935, **136**, 755). This permits us to deduce that the hydroxyl group in cevanthrol is most probably placed at one end of the molecule, preferably in position 3.

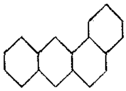
The crystallography of cevanthridine presents certain problems, since, although the halvings present were those of the monoclinic space group $P2_1/a$, no departure could be observed from orthorhombic symmetry. The photographs were, however, not very good, since the crystals grown from the melt were very imperfectly formed. As in the case of the aromatic hydrocarbons obtained in a similar way from the sterols, it is probable that these crystals consist of multiple twins and therefore can simulate orthorhombic symmetry. It is also just possible that the *c* dimension is double that recorded, since the photographs about [001] gave such blurred reflections that it was difficult to distinguish the true identity period. The crystal structure would then be very closely similar to that of the metastable modification of the hydrocarbon $C_{26}H_{26}$ from ergosterol, to which in any case it appears to have some relations.

The doubt as to the actual symmetry of the crystals does not affect the determination of the approximate arrangement of the molecules in the cell, since this is clearly indicated by the optic orientation and the marked intensity variations of the reflections, particularly the exceedingly strong fourth order of the *b* plane. From these data we may deduce the presence of molecules of dimensions approximately 17 × 6·8 × 3·8 Å. arranged with their lengths along *c* (γ), widths in *a* (β), and thickness four times over in *b* (α). This agrees further with the marked *b* cleavage.

The most plausible chemical structure for cevanthridine in agreement with these dimensions would appear to be one based on a condensed ring system of either type (I) or (II).

(I.)





(II.)

We reserve further discussion of these substances until more is known about their chemistry; but we wish to emphasise the mildness of the conditions employed in the dehydrogenation. Ruzicka and Peyer (*Helv. Chim. Acta*, 1935, **18**, 676) have shown that both α- and β-methylhydrindene are stable when heated with selenium below 400°, but at 450° ring enlargement to naphthalene occurs. Since the dehydrogenation of cevine was carried out at 320—330°, it seems likely that the ring systems of cevanthrol and cevanthridine largely exist ready-formed in cevine.

Experimental.

Cevanthrol.—Hydrated cevine (15 g.) and selenium (30 g.) were heated together in a 50 c.c. flask under the conditions previously described (*loc. cit.*). After cooling, ether was added, and the flask kept for 1—2 hours with occasional shaking. The ethereal extract was decanted, and the residue shaken several times with small quantities of fresh ether. The united extracts were filtered, and shaken first with dilute hydrochloric acid, whereby cevanthridine was removed as the insoluble hydrochloride, and then several times with aqueous alkali. The alkaline extracts were brilliant blue-green and gave no crystalline material on acidification. Finally, the ethereal solution was washed with water, dried, and evaporated, and the residue crystallised from benzene, giving cevanthrol in almost colourless crystals, m. p. 190—193°. By heating the selenium residues for a second period of 15 hours, and working up as before, further small amounts of both base and phenol were obtained. The final yield was 1·3—1·4 g. of cevanthridine picrate and 0·27—0·29 g. of cevanthrol. The regulus remaining after the second heating was powdered and extracted, but no crystalline material could be isolated.

Cevanthrol, after repeated crystallisation from benzene, formed rosettes of colourless plates, m. p. 197—198° (Found: C, 86·5; H, 6·7. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%). It was insoluble in cold aqueous alkali, but dissolved on heating.

The *acetate* was prepared by boiling a solution of the phenol (65 mg.) in acetic anhydride (1·5 c.c.) for 3 hours, and then adding water (0·7 c.c.) gradually to the hot solution. On scratching, the acetyl compound separated; it was recrystallised twice from acetic acid, forming thin diamond-shaped plates, m. p. 138—139° (Found: C, 82·0; H, 6·4. $C_{19}H_{18}O$ requires C, 82·0; H, 6·5%).

Morphology of Cevanthrol.—The small leaf-shaped plates of cevanthrol were elongated along *a* and showed only the (001) face. The plane of the optic axes is (010) with γ inclined at about 20° to the normal to the *c* plane. The birefringence is medium, positive and the optic axial angle fairly large.

Oscillation photographs were taken about the *a* axis.

Morphology of Cevanthridine.—Cevanthridine was obtained from solution as very minute, thin plates. Recrystallisation for *X*-ray work was effected by melting and recooling a small sample on a cover-slip under a heat gradient produced by means of a hot wire. The substance then crystallised in sheets on (001), which showed a very marked *b* cleavage. This made it easy to break off needle-shaped fragments for further measurement. Through the *c* face a biaxial figure was visible which showed a very close approximation to orthorhombic symmetry, with γ normal or nearly normal to (001), α along *b*, β along *a*. The birefringence was high, positive and the optic axial angle medium.

Oscillation photographs were taken about all three axes.

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98. *The Isomeric* 1-*Carboxy*-4-, -3-, *and* -2-*methyl*cyclo*hexane*-1-*acetic Acids.*

By R. D. Desai, R. F. Hunter, Ghulam Khan, and G. S. Saharia.

Hydrolysis of ethyl 1-cyano-4-methyl*cyclo*hexane-1-α-cyanoacetate, prepared by Higson and Thorpe's method (*J.*, 1906, **89**, 1455), produced two 1-carboxy-4-methyl*cyclo*hexane-1-acetic acids, m. p. 137° and 173°, identical with the two acids previously obtained by oxidation of the isomeric α-keto-4-methyl*cyclo*hexane-1 : 1-diacetic acids (Desai, J., 1932, 1057). As Qudrat-i-Khuda (*J. Indian Chem. Soc.*, 1931, **8**, 277) claims to have obtained four acids by hydrolysis of the above ester, his work was repeated. The acids he describes as (A), (B), and (C) were isolated in accordance with his directions, but the fourth isomeride was not obtained. The acids (A) and (C), m. p. 137° and 173° respectively, were identical with the two acids mentioned above, but the " acid (B)," as has already been shown by Goldschmidt and Grafinger (*Ber.*, 1935, **68**, 279), whose paper appeared before the completion of our experiments, was a mixture of (A) and (C).

The anhydrides of the two 1-carboxy-4-methyl*cyclo*hexane-1-acetic acids on condensation with benzene gave, in addition to the expected 1-*benzoyl*-4-*methyl*cyclo*hexane*-1-*acetic acids* (I), which were characterised by their *semicarbazones*, neutral products to which the formula (IV) is assigned, it being assumed that they are produced from the alternative products of condensation (II) by dehydration of the intermediate hydroxy-lactones (III) under the influence of hydrogen chloride.

$$\text{(I.)}\quad CHMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}COPh\\ CH_2\cdot CO_2H\end{matrix}\qquad CHMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CO_2H\\ CH_2\cdot COPh\end{matrix}\quad\text{(II.)}$$

$$\text{(III.)}\quad CHMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CO\text{---}O\\ CH_2\text{---}CPh\cdot OH\end{matrix}\qquad CHMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CO\text{---}O\\ CH{=}CPh\end{matrix}\quad\text{(IV.)}$$

Support is lent to this view by the observation that α-phenylsuccinic anhydride gives a mixture of β-benzoyl-α-phenyl- and β-benzoyl-β-phenyl-propionic acid on condensation with benzene in the presence of aluminium chloride (unpublished results).

Synthesis of the 1-carboxy-3-methyl*cyclo*hexane-1-acetic acids both by Higson and Thorpe's method and by that of Lapworth and McRae (J., 1922, **121**, 2741) gave two isomerides, a somewhat sharp-melting mixture of which was at first mistaken for a third form of the acid (Desai and Hunter, *Nature*, **1935**, **135**, 434).

Particular interest attaches to the synthesis of the 1-carboxy-2-methyl*cyclo*hexane-1-acetic acids in view of Thorpe's suggestion (J., 1931, 1023) that Qudrat-i-Khuda's second pair of acids might have arisen from the presence of 2-methyl*cyclo*hexanone in his 4-methyl*cyclo*hexanone. The melting points of the two 1-carboxy-2-methyl*cyclo*hexane-1-acetic acids obtained by both synthetic methods are quite different, however, from those of the acids (B) and (D) described by this author.

Experimental.

1-*Carboxy*-4-*methyl*cyclo*hexane*-1-*acetic Acids*.—(a) *Higson and Thorpe's method.* 4-Methyl*cyclo*hexanone (30 g.) was added to sodium bisulphite (26 g.) in water (100 c.c.) previously treated with sulphur dioxide. The oil which separated on addition of potassium cyanide (16 g. in 40 c.c. of water) was extracted in ether, dried (sodium sulphate), recovered, treated with two drops of concentrated sulphuric acid, and distilled under reduced pressure, 1-*hydroxy*-1-*cyano*-4-*methyl*cyclo*hexane* (30 g.) being obtained, b. p. 128°/20 mm. (Found : C, 68·9; H, 9·5. $C_8H_{13}ON$ requires C, 69·1; H, 9·3%). The cyanohydrin (16 g.) was gradually added to a solution of ethyl sodiocyanoacetate (sodium, 2·3 g.; absolute alcohol, 30 c.c.; ethyl cyanoacetate, 14 g.) and after 12 hours the mixture was heated on a water-bath for an hour and diluted with water. The oil produced was extracted and dried in ether and distilled, ethyl 1-cyano-4-methyl*cyclo*hexane-1-α-cyanoacetate passing over at 162—164°/15 mm. (Found: C, 66·4; H, 7·8. Calc. for $C_{13}H_{18}O_2N_2$: C, 66·7; H, 7·7%). Yield, 70%. The ester and concentrated hydrochloric acid (50 c.c.) were heated for 15 hours and the product was extracted

in ether and shaken with aqueous sodium carbonate. The alkaline layer on acidification with concentrated hydrochloric acid gave a mixture of acids (12 g.), m. p. 120—136°. This was extracted with hot benzene (50 c.c.); the residue (m. p. 160—165°), recrystallised from benzene, yielded 1-carboxy-4-methyl*cyclo*hexane-1-acetic acid, m. p. 173° (efferv.). The benzene extract, on cooling, deposited a product, m. p. 140—160°, which on further extraction with hot benzene furnished more of the acid, m. p. 173°. The benzene mother-liquor from the acid of m. p. 140—160°, after being concentrated, furnished 1-carboxy-4-methyl*cyclo*hexane-1-acetic acid, m. p. 132—134°, and 137° after recrystallisation.

(b) *Lapworth and McRae's method.* The yield of ethyl 4-methyl*cyclo*hexylidenecyanoacetate obtained from ethyl cyanoacetate and 4-methyl*cyclo*hexanone in presence of piperidine was improved by the addition of anhydrous sodium sulphate and heating for 24 hours. The unsaturated ester was condensed with potassium cyanide according to the directions of Qudrat-i-Khuda, the product heated with concentrated hydrochloric acid for 15 hours, and the mixture of acids isolated in the usual way. The ethereal solution gave the imide of the acid of m. p. 173°, which crystallised from dilute alcohol in plates, m. p. 171°; the mother-liquor yielded the imide, m. p. 128—129° after several recrystallisations, of the acid of m. p. 137°.

Separation of the Acids by Qudrat-i-Khuda's Method.—The crude mixture of acids was neutralised with ammonia, the solution evaporated to dryness, and the residue extracted with absolute alcohol. An aqueous solution of the insoluble portion was acidified with hydrochloric acid and extracted with ether, the product heated with acetic anhydride for 3 hours, the excess removed, and the residue distilled under reduced pressure, a mixture of anhydrides passing over at 165—180°/39 mm., which set to a crystalline mass, m. p. 55—58°. On recrystallisation from light petroleum (b. p. 60—80°), this gave an anhydride in lustrous white laminæ, m. p. 104°, derived from the acid of m. p. 173°, and thereafter a second anhydride in thick plates, m. p. 77°, which yielded the 1-carboxy-4-methyl*cyclo*hexane-1-acetic acid of m. p. 137° on being treated with water. The mother-liquor furnished a solid, m. p. 57—61°, from which a pure individual could not be obtained by recrystallisation, but which, on decomposition with water, gave an acid, m. p. 129° (with previous sintering); this was shown to be an impure specimen of the acid of m. p. 137° (mixed m. p. 132—134°) by the preparation of derivatives.

The ammonium salts recovered from the alcoholic extract (above) were heated with concentrated hydrochloric acid for 4—5 hours; the product, m. p. 145—155°, on extraction with benzene, gave the acid of m. p. 173°. The mother-liquor deposited impure fractions and, after concentration to small bulk, the acid of m. p. 137°. From the impure fractions, the acid, m. p. 173°, was isolated, but no evidence of an acid, m. p. 146°, was obtained.

Derivatives of the Anhydride, m. p. 104°.—The *imide* crystallised from dilute alcohol in leafy plates, m. p. 171° (Found: C, 66·1; H, 8·3. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3%), and the *amic acid* in plates, m. p. 195° (Found: C, 60·2; H, 8·7. $C_{10}H_{17}O_3N$ requires C, 60·4; H, 8·5%). The anilic acid crystallised in needles, m. p. 186°, and the anil had m. p. 185° (Qudrat-i-Khuda, *loc. cit.*). The p-*toluidinic acid* separated from dilute alcohol in needles, m. p. 168—169° (Found: C, 70·9; H, 8·0. $C_{17}H_{23}O_3N$ requires C, 70·6; H, 7·9%), the p-*tolylimide* in needles, m. p. 160° (Found: C, 75·6; H, 7·8. $C_{17}H_{21}O_2N$ requires C, 75·3; H, 7·8%), the *α-naphthylamic acid* in small plates, m. p. 140° (Found: C, 74·2; H, 7·1. $C_{20}H_{23}O_3N$ requires C, 73·8; H, 7·0%), and the *α-naphthylimide* formed needles, m. p. 163° (Found: C, 78·5; H, 6·9. $C_{20}H_{21}O_2N$ requires C, 78·4; H, 6·8%); the *β-naphthylamic acid* (Found: C, 74·1; H, 6·9%) and the *β-naphthylimide* (Found: C, 78·7; H, 6·8%) both had m. p. 185°, but the mixed m. p. was 165—170°.

Derivatives of the Anhydride, m. p. 77°.—The imide separated from dilute alcohol in plates, m. p. 130° (Qudrat-i-Khuda gives m. p. 119—120°), and the anilic acid in needles, m. p. 190°.

Derivatives of the Anhydride, m. p. 57—61°.—The imide after one crystallisation had m. p. 130°, undepressed by the imide of the acid of m. p. 137°. The anilic acid had m. p. 183° (previous sintering), and, after two recrystallisations, 190°, undepressed by the anilic acid obtained from the anhydride of m. p. 77°.

Condensation of the Anhydride, m. p. 104°, *with Benzene.*—A mixture of aluminium chloride (6·1 g.) and the anhydride (4·5 g.) in dry benzene, after being kept at laboratory temperature for 24 hours, was heated on a water-bath until the evolution of hydrogen chloride ceased. The residue obtained after removal of benzene was treated with cold dilute hydrochloric acid, and the residue from this was extracted with aqueous sodium carbonate (10%). On acidification of the extract, 1-*benzoyl*-4-*methyl*cyclo*hexane*-1-*acetic acid* (*A*) was obtained, which crystallised from benzene–petroleum in thick plates, m. p. 165° (Found: C, 73·4; H, 7·6; equiv., 258. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%; equiv., 260). The *semicarbazone* crystallised from alcohol

in thick plates, m. p. 165° (Found: C, 64·0; H, 7·5. $C_{17}H_{23}O_3N_3$ requires C, 64·3; H, 7·3%). The neutral *compound* left after the extraction with aqueous sodium carbonate separated from alcohol in needles, m. p. 160° (Found: C, 78·9; H, 7·4. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%); mixed m. p. with the acid (A) 135—139°.

Reduction of 1-*Benzoyl*-4-*methyl*cyclo*hexane*-1-*acetic Acid* (*A*).—A mixture of the keto-acid (4 g.), amalgamated zinc (30 g.), and concentrated hydrochloric acid (35 c.c.) was boiled for 24 hours and kept at laboratory temperature for 2 hours. After removal of the excess of zinc, the mixture was extracted with ether, and 1-*benzyl*-4-*methyl*cyclo*hexane*-1-*acetic acid* (*A*) isolated by extraction with aqueous sodium carbonate; it crystallised from light petroleum in soft needles, m. p. 98° (Found: C, 77·9; H, 9·1; equiv., 245. $C_{16}H_{22}O_2$ requires C, 78·0; H, 9·0%; equiv., 246).

1-*Benzoyl*-4-*methyl*cyclo*hexane*-1-*acetic acid* (*B*), prepared from the anhydride of m. p. 77° and benzene, crystallised from petroleum in thick plates, m. p. 140—141° (Found: C, 73·5; H, 7·8%; equiv., 261); the *semicarbazone* separated from alcohol in plates, m. p. 150° (Found: C, 64·1; H, 7·6%). The neutral *compound* formed in the Friedel-Crafts reaction crystallised from dilute alcohol in plates, m. p. 89° (Found: C, 79·2; H, 7·3%). Reduction of the acid (B) by Clemmensen's method furnished 1-*benzyl*-4-*methyl*cyclo*hexane*-1-*acetic acid* (*B*), which crystallised from light petroleum in needles, m. p. 127° (Found: C, 77·7; H, 8·9%); the ethereal solution which had been extracted with aqueous sodium carbonate furnished a neutral *compound*, which crystallised in prismatic needles, m. p. 250° (Found: C, 78·5; H, 8·1. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·2%).

1-*Carboxy*-3-*methyl*cyclo*hexane*-1-*acetic Acids*.—(a) *Higson and Thorpe's method.* The preparative details are similar to those described for the 4-methyl compounds. 1-*Hydroxy*-1-*cyano*-3-*methyl*cyclo*hexane*, prepared from 3-methyl*cyclo*hexanone (yield, 80%), had b. p. 120°/15 mm. (Found: C, 68·8; H, 9·2%). *Ethyl* 1-*cyano*-3-*methyl*cyclo*hexane*-1-α-*cyano-acetate*, obtained from it (17 g.) and ethyl sodiocyanoacetate (sodium, 3 g.; alcohol, 40 c.c.; ethyl cyanoacetate, 15 g.), had b. p. 185°/15 mm. (Found: C, 66·5; H, 7·9. $C_{13}H_{18}O_2N_2$ requires C, 66·7; H, 7·7%). Yield, 75%. The dicyano-ester was heated with concentrated hydrochloric acid (3 vols.) for 48 hours. The acidic products, isolated by means of ether and aqueous sodium carbonate, became semi-solid on keeping, and on treatment with benzene furnished 1-carboxy-3-methyl*cyclo*hexane-1-acetic acid, m. p. 163° (efferv.), identical with the acid obtained by oxidation of α-keto-3-methyl*cyclo*hexane-1 : 1-diacetic acid with hydrogen peroxide (Desai, *loc. cit.*). The gum obtained by evaporation of the benzene mother-liquor was treated with excess of aqueous ammonia (*d* 0·880) and heated with the calculated amount of aqueous barium chloride. The precipitated barium salt on decomposition with dilute hydrochloric acid furnished an oily product, which yielded the acid, m. p. 163°, on treatment with benzene. The filtrate from the barium salt on acidification deposited an oil, which was isolated by means of ether; when triturated with benzene, it solidified, m. p. 85—90°. On treatment with petroleum (b. p. 60—80°) most of it dissolved, leaving a residue of the acid, m. p. 163°. The petroleum extract on slow evaporation deposited a second 1-*carboxy*-3-*methyl*-cyclo*hexane*-1-*acetic acid*, which crystallised from benzene in plates, m. p. 108° (Found: C, 59·9; H, 8·1. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%. Found for the *silver* salt: Ag, 52·0. $C_{10}H_{14}O_4Ag_2$ requires Ag, 52·2%). A mixture of this acid with the acid, m. p. 163°, melted at 90—92°.

(b) *Lapworth and McRae's method.* Solutions of ethyl 3-methyl*cyclo*hexylidenecyanoacetate (50 g., b. p. 170°/15 mm.; for improved yield, see p. 417) in rectified spirit (225 c.c.) and of potassium cyanide (32 g.) in water (75 c.c.) were mixed and kept for 24 hours. The product obtained on removal of the alcohol was heated with concentrated hydrochloric acid (100 c.c.) for 48 hours, and the resulting gum extracted with ether. The semi-solid mixture of acids isolated by means of aqueous sodium carbonate was treated with benzene, the acid, m. p. 163°, being obtained. The benzene mother-liquor deposited a further quantity of this acid, and the gummy residue, by the ammonia-barium chloride treatment, also yielded this isomeride. The gum obtained from the soluble barium salt gave, on fractional crystallisation from petroleum-benzene, a solid (m. p. 75—85°), which, recrystallised from petroleum, furnished the isomeric acid, m. p. 108°. The mother-liquor gave a substance (2 g.) containing nitrogen, m. p. 181°, which yielded the acid, m. p. 108°, on hydrolysis with concentrated hydrochloric acid.

Derivatives of the Acid, m. p. 163°.—The anhydride had b. p. 150°/15 mm., and solidified in a freezing mixture; m. p. 41°. The anilic acid and the anil had m. p. 176° (efferv.) and m. p. 143° respectively (Desai, *loc. cit.*). The *imide* crystallised from dilute alcohol in plates, m. p. 180—181° (Found: C, 66·3; H, 8·4. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3%), the p-*toluidinic*

acid in needles, m. p. 180° (efferv.) (Found: C, 70·8; H, 8·1. $C_{17}H_{23}O_3N$ requires C, 70·6; H, 7·9%), the p-*tolylimide* in small needles, m. p. 145° (Found: C, 75·5; H, 7·9. $C_{17}H_{21}O_2N$ requires C, 75·3; H, 7·8%), the α-*naphthylamic acid* in needles, m. p. 150° (Found: C, 74·0; H, 7·2. $C_{20}H_{23}O_3N$ requires C, 73·8; H, 7·0%), the α-*naphthylimide* had m. p. 142° (Found: C, 78·6; H, 7·0. $C_{20}H_{21}O_2N$ requires C, 78·4; H, 6·8%), the β-*naphthylamic acid* separated from alcohol in needles, m. p. 192° (efferv.) (Found: C, 74·2; H, 6·9%), and the β-*naphthylimide* formed plates, m. p. 189° (Found: C, 87·7; H, 6·8%). A mixture of the last and the β-naphthylamic acid melted at 165—170°.

Derivatives of the Acid, m. p. 108°.—The *anhydride* had b. p. 145—148°/15 mm. and crystallised from hexane in prismatic needles, m. p. 50° (Found: C, 66·1; H, 7·8. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%). The *anilic acid* crystallised from alcohol in needles, m. p. 207° (Found: C, 69·7; H, 7·8. $C_{16}H_{21}O_3N$ requires C, 69·8; H, 7·6%); the *anil* had m. p. 107° (Found: C, 74·5; H, 7·5. $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4%). The *imide* separated from petroleum in needles, m. p. 92° (Found: C, 66·1; H, 8·5%). The p-*toluidinic acid* crystallised in needles, m. p. 185° (Found: C, 70·8; H, 7·8%); the *tolylimide* had m. p. 102—103° (Found: C, 75·5; H, 8·0%). The α-*naphthylamic acid*, m. p. 207° (Found: C, 73·5; H, 7·1%), the α-*naphthylimide*, m. p. 115° (Found: C, 78·1; H, 6·8%), and the β-*naphthylamic acid*, m. p. 183° (Found: C, 73·7; H, 7·3%), all crystallised in needles; the β-*naphthylimide* had m. p. 116° (Found: C, 78·5; H, 6·9%).

1-*Carboxy*-2-*methyl*cyclo*hexane*-1-*acetic Acids.*—1-*Hydroxy*-1-*cyano*-2-*methyl*cyclo*hexane* (28 g.), prepared from 2-methyl*cyclo*hexanone (28 g.), distilled at 114—116°/15 mm. (Found: C, 69·0; H, 9·4. $C_8H_{13}ON$ requires C, 69·1; H, 9·3%). *Ethyl* 1-*cyano*-2-*methyl*cyclo*hexane*-1-α-*cyanoacetate*, obtained in 50% yield from this ester and ethyl sodiocyanoacetate by the usual method, had b. p. 180°/15 mm. (Found: C, 66·4; H, 8·0. $C_{13}H_{18}O_2N_2$ requires C, 66·7; H, 7·7%). The dicyano-ester (20 g.) was heated with concentrated hydrochloric acid (50 c.c.) for 72 hours. The acids produced were extracted with ether, worked up in the usual way, and treated with benzene, a sparingly soluble 1-*carboxy*-2-*methyl*cyclo*hexane*-1-*acetic acid* being obtained, which crystallised from water in plates, m. p. 170° (efferv.) (Found: C, 59·9; H, 8·0; equiv., 101. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%; equiv., 100) [anhydride, b. p. 142—143°/12 mm.; *anilic acid*, thick cubes, m. p. 148°, from dilute alcohol (Found: C, 69·8; H, 7·7. $C_{16}H_{21}O_3N$ requires C, 69·8; H, 7·6%)]. More of this acid was obtained on concentration; the mother-liquor from this, on being kept for 24 hours, yielded a second *acid*, which separated from hot water in thick needles, m. p. 160° (Found: C, 60·2; H, 8·0%; equiv., 102), mixed m. p. with the first isomeride 135—140°. The anhydride of the second acid had b. p. 141—142°/12 mm., and the *anilic acid* separated from dilute alcohol in slender needles, m. p. 161—162° (Found: C, 70·1; H, 7·6%).

Ethyl 2-*Methyl*cyclo*hexylidenecyanoacetate.*—A mixture of 2-methyl*cyclo*hexanone (40 c.c.), ethyl cyanoacetate (35 c.c.), and piperidine (8—10 drops) was kept for 24 hours and, after addition of anhydrous sodium sulphate, heated for 48 hours. The unsaturated *ester* distilled at 150—160°/15 mm. (Found: C, 69·4; H, 8·4. $C_{12}H_{17}O_2N$ requires C, 69·6; H, 8·2%). Yield, 50%. The unsaturated ester (25 g.) in rectified spirit (100 c.c.) was treated with potassium cyanide (16 g. in 40 c.c. of water), and the mixture was hydrolysed by heating with concentrated hydrochloric acid (75 c.c.) for 48 hours. From the acidic portion, worked up in the usual way, the two isomeric 1-carboxy-2-methyl*cyclo*hexane-1-acetic acids already described were obtained.

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99. *Experiments on the Synthesis of Rotenone and its Derivatives. Part IX.*

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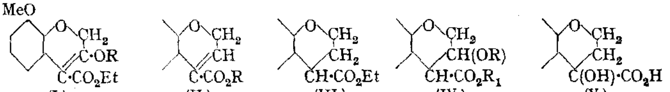
THE experiments described in this communication were undertaken in our search of intermediates for preliminary experiments on the synthesis of compounds of the rotenol type and of the chromano-chromanone nucleus of rotenone which appears to be feasible by way of the netoric acid and toxicaric acid types. Although the synthesis of the latter acids proceeded smoothly with comparatively good yields (Part VIII; this vol., p. 212), the difficulty of obtaining the initial materials in quantity led us to explore the preparation of analogous acids. Accordingly, the preparation of 7- and 8-methoxychroman-4-carboxylic

acid and of 7- and 8-methoxy-Δ^3-chromene-4-carboxylic acid has now been achieved by the route employed for netoric acid and toxicaric acid and differing from the latter only in experimental details. Because of the poor yields of ethyl 3-hydroxy-Δ^3-chromene-4-carboxylate obtained by cyclisation of ethyl phenoxyacetate-2-acetate (Mr. W. Hilton of this Laboratory, private communication) the investigation of the unsubstituted analogues has not been proceeded with.

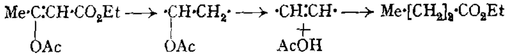
Application of the cyanohydrin method (Part VI; J., 1935, 995) to the production of the intermediate *6-methoxyphenoxyacetic-2-acetic acid* gave disappointing results and we returned to a modification of the standard procedure employed for the synthesis of derric acid (Part II; J., 1932, 1380). Attempts to utilise the cyanohydrin route for the preparation of the corresponding resorcinol derivative were also unsuccessful, because, although ethyl 5-methoxy-2-aldehydophenoxyacetate yields a comparatively stable cyanohydrin by the usual methods, efforts to replace the hydroxyl group by chlorine with the aid of thionyl chloride or phosphorus pentachloride in an inert solvent led to the formation of resinous products.

Hydrolysis of esters of the type (IV) with alkali is accompanied by dehydration with the formation of unsaturated acids (type II) (compare Part VIII, *loc. cit.*), but we have also found in the case of (IV; R = Ac, R_1 = Et) that hydrolysis with dilute hydrochloric acid gives rise to the *hydroxy-acid* (IV; R = H, R_1 = H), an analogue of hydroxynetoric acid. Unlike the *ester* (IV; R = H, R_1 = Et), which on being warmed with acetic anhydride gives an almost quantitative yield of the *acetate* (IV; R = Ac, R_1 = Et), the acid (IV; R = H, R_1 = H) is dehydrated with acetic anhydride–pyridine mixture even at room temperature, forming the *chromeno-acid* (II, R = H). Hydrolysis of the *ester* (IV; R = Ac, R_1 = Et) with dilute hydrochloric acid might conceivably have given rise to an isomeric acid (V) by a process of dehydration and subsequent hydration, but this possibility is excluded by the fact that on esterification with diazoethane the hydroxy-acid forms the ester (IV; R = H, R_1 = Et).



(I.) (II.) (III.) (IV.) (V.)

The marked difference in the course taken by the enols (compare Michael and Ross, *J. Amer. Chem. Soc.*, 1931, 53, 2394) and their acetates on hydrogenation, upon which the success of these syntheses depends, is of some interest and in their memoir on the reduction of enol-acetates Roll and Adams (*ibid.*, p. 3469) suggest that the course of the reaction is as follows:



Although the reduction of the acetate (I, R = Ac) to the chroman-ester (III) proceed smoothly even at atmospheric pressure, we found that the acetate (IV; R = Ac, R_1 = Et could not be converted directly into (III), and it would therefore appear that, contrary t the suggestion of Roll and Adams, the acetate (IV; R = Ac, R_1 = Et) as such is not a intermediate in the conversion of type (I, R = Ac) into type (III). Although, as suggeste by these authors, there is the possibility of a direct reduction of (I, R = Ac) to (III), it ma well be that the first stage of this conversion is the extrusion of acetic acid with the forr ation of (II, R = Et), which is immediately hydrogenated to (III).

Experimental

6-Methoxyphenoxyacetic-2-acetic Acid.—The following procedure gave satisfactory yields the acid and avoided the troublesome isolation of 6-methoxyphenoxyacetic-2-pyruvic ac (Part VI, *loc. cit.*). A mixture of the azlactone of ethyl 2-aldehydo-6-methoxyphenoxyaceta (20 g.) and 10% aqueous sodium hydroxide (200 c.c.) was refluxed for 4 hours and diluted wi

water (50 c.c.), and the greater part of the benzoic acid removed with the aid of sulphur dioxide in the usual manner; a small amount of benzoic acid which remained in solution was removed with ether. The aqueous liquor was heated on the steam-bath with concentrated hydrochloric acid (50 c.c.) for 1 hour to decompose the bisulphite compound of the pyruvic acid and to remove dissolved sulphur dioxide; it was then cooled, basified with powdered sodium hydroxide, and treated with 30% hydrogen peroxide (6 c.c., added in the course of 15 minutes with cooling). One hour later the mixture was heated at 50—55° for 20 minutes, and *6-methoxyphenoxyacetic-2-acetic acid* precipitated from the cooled solution by means of sulphur dioxide. Crystallised from warm water, the acid formed diamond-shaped plates (8 g.), m. p. 166°, sparingly soluble in benzene or light petroleum (Found: C, 55·0; H, 5·0. $C_{11}H_{12}O_6$ requires C, 55·0; H, 5·0%). Esterified with alcohol and sulphuric acid, it gave the ethyl ester as a colourless viscous oil, b. p. 198—200°/11 mm. The same ester, mixed with a small amount of free acid, was also obtained by boiling ethyl 6-methoxyphenoxyacetate-2-acetonitrile (10 g., prepared by the cyanohydrin method; Part VI, *loc. cit.*) with alcohol (50 c.c.) and sulphuric acid (25 c.c.), but this route was less satisfactory than the foregoing procedure.

Ethyl 3-Hydroxy-8-methoxy-Δ³-chromene-4-carboxylate (I, R = H).—Cyclisation of the afore-mentioned ester (5 g.) was effected with powdered sodium (0·6 g.) in warm benzene (50 c.c.) in the course of 2 hours. The cooled reaction mixture was treated with water, the benzene separated with the aid of ether, and the aqueous liquor acidified with concentrated hydrochloric acid. Next day the almost pure *product* (2·8 g.) was collected, washed, dried, and crystallised from light petroleum (b. p. 60—80°), forming colourless, stout, rectangular prisms, m. p. 87°, readily soluble in cold aqueous sodium hydroxide and giving a stable royal-blue coloration with alcoholic ferric chloride (Found: C, 62·2; H, 5·8. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6%). Prepared by the pyridine–acetic anhydride method, the *acetate* separated from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 72°, with negative ferric reaction (Found: C, 61·7; H, 5·5. $C_{15}H_{16}O_6$ requires C, 61·6; H, 5·5%).

Hydrolysis of the enol-ester with 10% aqueous sodium hydroxide at room temperature for 12 hours gave rise to 6-methoxyphenoxyacetic-2-acetic acid, m. p. and mixed m. p. 166°.

8-Methoxychroman-4-carboxylic Acid.—Reduction of ethyl 3-acetoxy-8-methoxy-Δ³-chromene-4-carboxylate (2 g.) was effected in acetic acid (40 c.c.) with hydrogen at 55 lb./sq. in. and a platinum catalyst (Adams) (0·1 g.) in the course of 15 hours. The filtered solution was diluted with water (250 c.c.) and neutralised with sodium carbonate. On isolation with ether the oily product was hydrolysed with 5% ethyl-alcoholic potassium hydroxide (20 c.c.) on the steam-bath for 2 hours and after the addition of water (20 c.c.) the greater part of the alcohol was distilled, and the *acid* precipitated from the cooled residue with concentrated hydrochloric acid. This substance formed clusters of irregular prisms (0·7 g.) from light petroleum (b. p. 80—100°), m. p. 110°, readily soluble in acetone, alcohol, or benzene (Found: C, 63·6; H, 5·7. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

It was subsequently discovered that the reduction of the acetate (1 g.) in acetic acid (20 c.c.) was slowly effected with the same catalyst (0·1 g.) and hydrogen at atmospheric pressure. After isolation and hydrolysis of the product the resulting acid was isolated with ether as a reddish-brown solid, from which pure material (0·2 g.) was obtained by extraction with boiling light petroleum and then crystallisation from same solvent; m. p. and mixed m. p. 110°.

Ethyl 3-Hydroxy-8-methoxychroman-4-carboxylate (IV; R = H, R_1 = Et).—Ethyl 3-hydroxy-8-methoxy-Δ³-chromene-4-carboxylate (2 g.) was reduced in alcohol (150 c.c.) with hydrogen (200 c.c. absorbed) at atmospheric pressure in the presence of a platinum catalyst (0·15 g.) in 4—6 hours. Evaporation of the filtered solution left the *ester* as a thick viscous oil, which gradually solidified and then separated from light petroleum (b. p. 60—80°) in clusters of rod-like prisms, m. p. 85°, readily soluble in alcohol or benzene, insoluble in aqueous sodium hydroxide, and having a negative ferric reaction (Found: C, 62·3; H, 6·4. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·4%). Treatment of this compound (2 g.) with acetic anhydride (10 c.c.) at 100° for 2 hours gave the *acetate* (IV; R = Ac, R_1 = Et), which separated from light petroleum (b. p. 40—60°) in irregular prisms (1·9 g.), m. p. 94°, identical with a specimen obtained by acetylation with the aid of pyridine at room temperature [Found: C, 61·6; H, 6·2; CH_3·CO, 16·3. $C_{13}H_{15}O_5(CO{\cdot}CH_3)$ requires C, 61·2; H, 6·1; CH_3·CO, 14·6%]. Attempts to reduce this derivative under conditions employed for the preparation of 8-methoxychroman-4-carboxylic acid were unsuccessful; *e.g.*, a solution of the ester (0·5 g.) in acetic acid (10 c.c.) containing an active platinum catalyst (0·1 g.) was agitated in hydrogen at 50 lb./sq. in. for 16 hours. Addition of water to the filtered solution quantitatively precipitated unchanged material, m. p. and mixed m. p. 94°.

3-*Hydroxy*-8-*methoxychroman*-4-*carboxylic Acid* (IV; R = H, R_1 = H).—Ethyl 3-acetoxy-8-methoxychroman-4-carboxylate (2 g.) was boiled with *N*-hydrochloric acid (30 c.c.) for 1·5 hours, and the resulting solution decanted from a small amount of tarry residue. The *hydroxy-acid* (1 g.) separated from the cooled solution; a further quantity (0·1 g.) was isolated from the acid liquors by means of ether. The compound formed colourless elongated prisms from acetone–light petroleum (b. p. 60—80°), m. p. 197° (decomp.) (Found in a specimen dried in a high vacuum at 100°: C, 59·1; H, 5·4. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%). Esterification of this acid with ethereal diazoethane gave ethyl 3-hydroxy-8-methoxychroman-4-carboxylate, m. p. 85°, identified by comparison with an authentic specimen.

8-*Methoxy*-Δ^3-*chromene*-4-*carboxylic Acid* (II, R = H).—Treatment of the foregoing hydroxy-acid (0·5 g.) with acetic anhydride (2 c.c.) and pyridine (1 c.c.) at room temperature for 24 hours gave rise to the *acid*, which separated from benzene or water in almost colourless, slender needles (0·3 g.), m. p. 170° (Found: C, 64·2; H, 5·0. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%). It is readily soluble in alcohol or acetic acid and instantaneously decolorises aqueous potassium permanganate or bromine water. The same acid resulted from the hydrolysis of ethyl 3-hydroxy-8-methoxychroman-4-carboxylate (0·5 g.) or its acetate with aqueous-alcoholic potassium hydroxide (from 0·4 g. of alkali, 2 c.c. of water, and 9 c.c. of alcohol) on the water-bath for 1 hour. The solution was diluted with an equal volume of water, the greater part of the alcohol distilled, and the compound (0·15 g.) precipitated with concentrated hydrochloric acid (cooling); m. p. 170° after crystallisation from water.

5-*Methoxyphenoxyacetic*-2-*acetic Acid*.—After exhaustive purification the initial material, ethyl 2-aldehydo-5-methoxyphenoxyacetate, had m. p. 64° as previously recorded (Part III, J., 1933, 489; Dumont and Kostanecki, *Ber.*, 1909, **42**, 911, give m. p. 68—69°).

This *acid* was prepared by the oxidation of 5-methoxyphenoxyacetic-2-pyruvic acid (Part III, *loc. cit.*) (2·5 g.) in 5% aqueous sodium hydroxide (20 c.c.) with 30% hydrogen peroxide (2 c.c.) and formed colourless prisms (2·0 g.) from warm water, m. p. 163°, readily soluble in alcohol and sparingly soluble in benzene or ethyl acetate (Found: C, 55·0; H, 5·1. $C_{11}H_{12}O_6$ requires C, 55·0; H, 5·0%). The *ethyl* ester was obtained as a crystalline solid, b. p. 178—180°/1 mm., m. p. 37° (Found: C, 61·0; H, 6·8. $C_{15}H_{20}O_6$ requires C, 60·8; H, 6·8%).

Ethyl 3-*Hydroxy*-7-*methoxy*-Δ^3-*chromene*-4-*carboxylate*.—Cyclisation of the afore-mentioned ester (10 g.) was effected with powdered sodium (1·2 g.) in warm benzene (75 c.c.) and on isolation the *product* (4·5 g.) crystallised from warm alcohol in colourless, thick, rectangular prisms, m. p. 62—63°, instantaneously soluble in dilute aqueous sodium hydroxide and giving a Prussian-blue ferric chloride reaction (Found: C, 62·1; H, 5·4. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6%). The *acetate*, obtained by means of acetic anhydride and pyridine, formed plates or needles from dilute alcohol, m. p. 51° (Found: C, 61·6; H, 5·5. $C_{15}H_{16}O_6$ requires C, 61·6; H, 5·5%).

7-*Methoxychroman*-4-*carboxylic Acid*.—Reduction of the afore-mentioned acetate (1 g.) in acetic acid (30 c.c.) with hydrogen at 45—50 lb./sq. in. and a platinum catalyst gave a colourless oil, which on hydrolysis with hot 4% alcoholic potassium hydroxide (15 c.c.) for 1½ hours yielded the *acid* as a dark brown oil. This material solidified in the course of 2—3 weeks and then separated from light petroleum (b. p. 40—60°) in colourless irregular prisms (0·3—0·4 g.), m. p. 78°, readily soluble in the usual solvents except light petroleum (Found: C, 63·6; H, 6·0. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

7-*Methoxy*-Δ^3-*chromene*-4-*carboxylic Acid*.—Hydrogenation of ethyl 3-hydroxy-7-methoxy-Δ^3-chromene-4-carboxylate (1 g.) in alcohol (100 c.c.) with hydrogen (approx. 100 c.c. absorbed) at atmospheric pressure and a platinum catalyst (0·1 g.) gave *ethyl* 3-*hydroxy*-7-*methoxychroman*-4-*carboxylate* (1 g.), which formed slender rods from light petroleum (b. p. 60—80°), m. p. 97° (Found: C, 62·2; H, 6·4. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·4%). This ester (1 g.) was heated with acetic anhydride (6 c.c.) on the steam-bath for 2 hours, and the oily product hydrolysed by being boiled with alcohol (22 c.c.) and water (4 c.c.) containing potassium hydroxide (0·8 g.) for ¾ hour. On isolation the *acid* separated from warm water in almost colourless needles (0·45 g.), m. p. 131°, readily soluble in alcohol and sparingly soluble in benzene or light petroleum (Found: C, 64·2; H, 5·2. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%). This compound instantaneously decolorised aqueous potassium permanganate or bromine water.

We are indebted to the Government Grants Committee of the Royal Society for a grant in aid of this work.

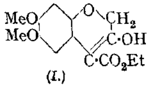
UNIVERSITY OF LIVERPOOL. [*Received, January 24th*, 1936.]

100. *Analogues of Rotenone and Related Compounds. Part I. Chromeno-(3′ : 4′ : 4 : 3)-coumarins.*

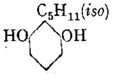
By William Hilton, Ronald W. H. O'Donnell, Firmin P. Reed, Alexander Robertson, and George L. Rusby.

It is well established that members of the rotenone group of natural compounds possess, in addition to other physiological properties, an exceptionally high degree of toxicity to fish and certain insects. Some of the related natural furanocoumarins of the bergapten type also are capable of acting as fish poisons and it appeared that an investigation of the toxicity of analogous pyrones, dihydropyrones, pyrans, and furano-compounds would yield results of considerable interest and would, if sufficiently extensive, contribute considerably to our knowledge of structure in relation to this particular aspect of physiological activity. Moreover the rotenone molecule is complex, comprising three heterocyclic systems, and little is known regarding the features which are essential for toxicity and those, if any, which may be considered to contribute an auxotoxic effect (compare Gersdorff, *J. Amer. Chem. Soc.*, 1930, **52**, 5051; 1933, **55**, 1147; 1934, **56**, 979). To this problem a study of compounds embodying one or more of the heterocyclic systems present in the rotenone molecule (*i.e.*, sections of the rotenone molecule) would appear to offer a fertile approach. Accordingly, we have initiated a comprehensive investigation on the synthesis of analogues of rotenone and related compounds with the object of making a comparative study of their physiological properties when a sufficiently representative range of substances has been obtained. This topic is cognate to experiments on the synthesis of rotenone which are proceeding in these laboratories.

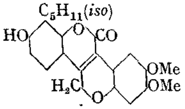
The present communication deals with the synthesis by general methods of a series of chromeno-(3′ : 4′ : 4 : 3)-coumarins (type III), some of which are isomeric with the chromeno-(3′ : 4′ : 2 : 3)-chromones previously described (Robertson, J., 1933, 489, 1163; King and Robertson, J., 1935, 993): as an example, the condensation of the enol-ester (I) with tetrahydrotubanol (II) according to the method of Pechmann gave rise to 7-*hydroxy*-6′ : 7′-*dimethoxy*-8-iso*amylchromeno*-(3′ : 4′ : 4 : 3)-*coumarin* (III), isomeric with tetrahydrodehydrorotenone (*loc. cit.*).



(I.)



(II.)



(III.)

The condensation of (I) and of ethyl 3-hydroxy-8-methoxy-Δ^3-chromene-4-carboxylate with phenols of the resorcinol type proceeded remarkably well by the sulphuric acid method. The failure to effect interaction between ethyl 3-hydroxy-7-methoxy-Δ^3-chromene-4-carboxylate and resorcinol or phloroglucinol by this means led us to employ alcoholic hydrogen chloride as the condensing agent, a procedure first used by Robinson and his co-workers (J., 1918, **113**, 879) and more recently extended by Appel (J., 1935, 1031), whose memoir appeared while the present work was in progress. Where comparison has been possible, the products obtained by the latter method are generally cleaner and the yields occasionally better.

The chromeno-(3′ : 4′ : 4 : 3)-coumarins are in general more intensely coloured and less soluble in organic solvents than the analogous chromenochromones of the dehydrorotenone type (*loc. cit.*). With concentrated sulphuric acid the coumarins derived from the ester (I) form dark red or purple solutions which become pale yellow on the addition of water, whereas those from ethyl 3-hydroxy-7-methoxy- and ethyl 3-hydroxy-8-methoxy-Δ^3-chromene-4-carboxylate form bright yellow solutions which, except that of 7-*hydroxy*-7′-*methoxy*-8-iso*amylchromeno*-(3′ : 4′ : 4 : 3)-*coumarin*, are non-fluorescent in daylight; the solution of the last coumarin exhibits an intense green fluorescence.

Experimental.

7-Hydroxy-6′ : 7′-dimethoxychromeno-(3′ : 4′ : 4 : 3)-coumarin.—(A) Resorcinol (0·7 g.) was gradually added to a solution of ethyl 3-hydroxy-6 : 7-dimethoxy-Δ^3-chromene-4-carboxylate (Robertson and Rusby, this vol., p. 212) (0·4 g.) in 85% sulphuric acid (7 c.c.) at 0° and the resulting dark brownish-red mixture was kept for 48 hours at room temperature; a considerable amount of crystalline material gradually separated. The mixture was poured on ice, the aqueous liquor saturated with ammonium sulphate, and next day the *coumarin* was collected, washed with a little water, and crystallised from dilute alcohol (charcoal), forming a *hydrate* (0·25 g.) in slender yellow needles, m. p. 245° with slight sintering at 240°, having a negative ferric reaction (Found in material dried in a vacuum at room temperature: C, 62·9; H, 4·6. $C_{18}H_{14}O_6,H_2O$ requires C, 62·8; H, 4·7%. Found in a specimen dried in a high vacuum at 120°: C, 65·9; H, 4·4. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%). The compound is readily soluble in acetone and aqueous sodium hydroxide and sparingly soluble in water, ethyl acetate, and acetic acid. Refluxed with acetic anhydride (5 c.c.) and sodium acetate (0·1 g.) for ½ hour, the coumarin (0·18 g.) yielded the *acetate* (0·13 g.), which separated from a large volume of alcohol in bright yellow, elongated plates, m. p. 220—221° (Found in material dried in a high vacuum at 120°: C, 65·6; H, 4·6. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4%). The use of pyridine and acetic anhydride at room temperature gave the same derivative.

(B) Dry hydrogen chloride was slowly led into a solution of the ester (0·8 g.) and resorcinol (1·2 g.) in methyl alcohol (20 c.c.) maintained at room temperature for 1 hour. The mixture was then heated at 50° for 5 minutes to redissolve a small amount of solid, cooled, saturated with hydrogen chloride, kept for 4 days, and warmed at 50° for 10 minutes. Next day the solid (0·3 g.) was collected, washed, and crystallised from dilute alcohol, forming yellow needles, m. p. and mixed m. p. 245° with sintering at 240°. The acetate had m. p. 220—221°, alone or mixed with an authentic specimen.

7 : 8-Dihydroxy-6′ : 7′-dimethoxychromeno-(3′ : 4′ : 4 : 3)-coumarin, prepared from the ester (0·4 g.) and pyrogallol (0·7 g.) with 85% sulphuric acid (7 c.c.), separated from dilute alcohol as a *hydrate* in yellow needles, m. p. 274° (decomp.) after sintering at 268°, sparingly soluble in water or hot benzene and readily soluble in acetone or warm ethyl acetate (Found in a specimen dried in a vacuum: C, 60·2; H, 4·5. $C_{18}H_{14}O_7,H_2O$ requires C, 60·0; H, 4·5%. Found in material dried in a high vacuum at 120°: C, 63·2; H, 4·2. $C_{18}H_{14}O_7$ requires C, 63·2; H, 4·1%). With aqueous sodium hydroxide this coumarin gives an orange solution and with alcoholic ferric chloride an olive-green coloration. The *diacetate* crystallised from much alcohol in aggregates of elongated yellow plates, m. p. 232—233° (Found: C, 61·7; H, 4·3. $C_{22}H_{18}O_9$ requires C, 62·0; H, 4·3%).

5 : 7-Diacetoxy-6′ : 7′-dimethoxychromeno-(3′ : 4′ : 4 : 3)-coumarin.—Prepared by the Pechmann method, the hydroxy-coumarin, which was only very sparingly soluble in the usual solvents, was not obtained analytically pure. On being concentrated, a solution of the reaction product in much alcohol (charcoal) deposited partly purified material in microscopic clusters of yellow needles, m. p. above 300°, readily soluble in alkali, having a negative ferric chloride reaction, and yielding the *diacetate*, which crystallised from acetic acid or a large volume of alcohol in bright yellow rods, m. p. 190° (Found: C, 62·0; H, 4·3. $C_{22}H_{18}O_9$ requires C, 62·0; H, 4·3%).

*7-Hydroxy-6′ : 7′-dimethoxy-8-*iso*amylchromeno-(3′ : 4′ : 4 : 3)-coumarin* was obtained from tetrahydrotubanol (Robertson, *loc. cit.*) (0·5 g.) and the ester (0·5 g.) with 85% sulphuric acid (8 c.c.), and separated from alcohol in bright yellow, irregular, elongated plates, m. p. 230—231°, readily soluble in acetone or ethyl acetate and having a negative ferric reaction (Found in material dried in a high vacuum at 120°: C, 69·4; H, 6·1. $C_{23}H_{24}O_6$ requires C, 69·7; H, 6·1%). The *acetate* formed lustrous, bright yellow plates, m. p. 137°, from alcohol (Found in material dried at 120° in a high vacuum: C, 68·5; H, 6·0. $C_{25}H_{26}O_7$ requires C, 68·5; H, 5·9%).

The following 7′-methoxychromenocoumarins were prepared from ethyl 3-hydroxy-7-methoxy-Δ^3-chromene-4-carboxylate (Robertson and co-workers, this vol., p. 422) by the alcoholic hydrogen chloride method. A solution of the ester (0·3 g.) and the requisite phenol (0·4 g.) in methyl alcohol (3 c.c.) was saturated with hydrogen chloride, kept for 2 days at room temperature, and warmed on the steam-bath for ½ hour. Twenty-four hours later, the crystalline product (0·2—0·25 g.) was collected and purified. The acetyl derivatives were prepared by means of warm acetic anhydride and pyridine.

7-Hydroxy-7′-methoxychromeno-(3′ : 4′ : 4 : 3)-coumarin separated from methyl alcohol

yellow rods, m. p. 266°, sparingly soluble in acetone and having a negative ferric reaction (Found in material dried in a high vacuum at 110°: C, 68·8; H, 4·1. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%). The *acetate* formed yellow rods, m. p. 222°, from acetic acid (Found: C, 67·4; H, 4·1. $C_{19}H_{14}O_6$ requires C, 67·4; H, 4·2%).

7 : 8 : *Dihydroxy-7′-methoxychromeno-*(3′ : 4′ : 4 : 3)-*coumarin* formed tiny yellow needles, m. p. 254°, from alcohol, soluble in acetone and giving an olive-green coloration with alcoholic ferric chloride (Found: C, 65·3; H, 3·9. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%). This coumarin was also prepared in small yield by means of 86% sulphuric acid. The *diacetate* crystallised from acetic acid in yellow needles, m. p. 231·5° (Found: 63·5; H, 3·9. $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·1%).

5 : 7-*Dihydroxy-7′-methoxychromeno-*(3′ : 4′ : 4 : 3)-*coumarin* separated from alcohol in yellow rods, m. p. 309°, soluble in acetone and having a negative ferric reaction (Found in material dried in a high vacuum at 110°: C, 65·1; H, 4·0. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%). The *diacetate* formed pale yellow rods from acetic acid, m. p. 253° (Found: C, 63·9; H, 4·2. $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·1%).

7-*Hydroxy-7′-methoxy-*8-iso*amylchromeno-*(3′ : 4′ : 4 : 3)-*coumarin* crystallised from alcohol in tiny yellow needles, m. p. 228°, soluble in acetone or acetic acid and having a negative ferric reaction (Found: C, 72·1; H, 6·0. $C_{22}H_{22}O_5$ requires C, 72·1; H, 6·0%). The yield of this coumarin was increased by about 60% when the condensation was carried out in ethyl instead of methyl alcohol. The *acetate* formed yellow rods, m. p. 219°, from acetic acid (Found: C, 70·4; H, 5·7. $C_{24}H_{24}O_6$ requires C, 70·6; H, 5·9%).

The condensation of ethyl 3-hydroxy-8-methoxy-Δ^3-chromene-4-carboxylate (Robertson and co-workers, *loc. cit.*) with resorcinol, pyrogallol, and phloroglucinol was carried out by the sulphuric acid method and by the alcoholic hydrogen chloride method (yields approximately the same); in the latter process it was found that when ethyl alcohol was replaced by methyl alcohol the yields diminished.

7-*Hydroxy-8′-methoxychromeno-*(3′ : 4′ : 4 : 3)-*coumarin* formed clusters of pale yellow needles, m. p. 269°, from much alcohol, having a negative ferric chloride reaction and giving an almost colourless solution in aqueous sodium hydroxide (Found: C, 68·6; H, 4·1. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%). The *acetate* crystallised from acetic acid in pale yellow needles, m. p. 232° (Found: C, 67·2; H, 4·1. $C_{19}H_{14}O_6$ requires C, 67·4; H, 4·2%).

7 : 8-*Dihydroxy-8′-methoxychromeno-*(3′ : 4′ : 4 : 3)-*coumarin* was obtained from acetic acid in slender, pale yellow prisms, m. p. 277°; the ferric chloride reaction was olive-green and the solution in aqueous sodium hydroxide orange-red (Found in a specimen dried at 120° in a high vacuum: C, 65·3; H, 3·9. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%). The *diacetate* formed clusters of pale yellow needles, m. p. 246° (decomp.) (Fonnd: C, 63·7; H, 4·2. $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·1%).

5 : 7-Dihydroxy-8′-methoxychromeno-(3′ : 4′ : 4 : 3)-coumarin could not be satisfactorily purified; dilution of an alcoholic solution with water gave clusters of yellow microscopic prisms decomposing at about 290°, having a negative ferric chloride reaction, and forming an orange solution in aqueous sodium hydroxide. The well-crystallised *diacetate* separated from acetic acid in pale yellow needles, m. p. 224° (Found: C, 63·4; H, 4·1. $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·1%).

7-*Hydroxy-8′-methoxy-*8-iso*amylchromeno-*(3′ : 4′ : 4 : 3)-*coumarin* (0·5 g.) was prepared from the requisite ester (0·5 g.) and tetrahydrotubanol (0·5 g.) in alcohol (6 c.c.) by means of hydrogen chloride in the course of 3 days, and crystallised from alcohol and then acetic acid, forming pale yellow needles, m. p. 245°, having a negative ferric reaction and giving a pale yellow solution in aqueous sodium hydroxide (Found in material dried at 110° in a high vacuum: C, 71·9; H, 5·7. $C_{22}H_{22}O_5$ requires C, 72·1; H, 6·0%). The *acetate* separated from alcohol in straw-coloured needles, m. p. 188° (Found: C, 70·8; H, 6·1. $C_{24}H_{24}O_6$ requires C, 70·6; H, 5·9%).

Phenoxyacetic-2-acetic Acid.—The initial material, ethyl 2-aldehydophenoxyacetate (Robertson, *loc. cit.*), for the preparation of phenoxyacetic-2-pyruvic acid has now been found, after repeated purification from light petroleum (b. p. 80—100°), to melt at 47—48° as stated by Dumont and Kostanecki (*Ber.*, 1909, **42**, 911).

(A) The azlactone of this aldehyde (Robertson, *loc. cit.*) (25 g.) was hydrolysed with boiling 10% aqueous sodium hydroxide (250 c.c.) in the course of 6 hours. After the addition of water (50 c.c.), the benzoic acid was removed in the usual manner with sulphur dioxide, concentrated hydrochloric acid (50 c.c.) added, and the mixture heated on the water-bath for 2 hours, basified with powdered sodium hydroxide (20 g.), treated at room temperature with 30% hydrogen peroxide (7 c.c., added gradually), kept for 1 hour, heated at 50—55° for 15 minutes, cooled,

and acidified with excess of sulphur dioxide. The phenoxyacetic-2-acetic acid thus precipitated was most conveniently purified with the aid of amyl ether, from which it separated in slender needles, m. p. 154—155°, unchanged by repeated purification (compare La Forge, *J. Amer. Chem. Soc.*, 1933, **55**, 3040, and Kostanecki and co-workers, *Ber.*, 1909, **42**, 827, who respectively give m. p. 154° and 158—159°). Esterification of this acid with hot alcohol and sulphuric acid gave an almost theoretical yield of the *ethyl* ester, which formed slender prisms, m. p. 48—49°, from light petroleum (b. p. 80—100°) (Found: C, 63·2; H, 6·9. $C_{14}H_{18}O_5$ requires C, 63·2; H, 6·8%).

(B) To a well-stirred mixture of the bisulphite compound of ethyl 2-aldehydophenoxyacetate (from 10 g. of aldehyde) in a saturated aqueous solution of sodium hydrogen sulphite (200 c.c.), sodium cyanide (5 g.) in water (10 c.c.) was added at 0° in the course of 1 hour, and 3 hours later the cyanohydrin was isolated with ether, being obtained as a colourless solid (7·2 g.), m. p. 64—65°. This compound (3 g.) was treated in chloroform (3 c.c.) with thionyl chloride (3 c.c., added slowly) and 24 hours later the solvent was evaporated, leaving the chloro-nitrile as a brown oil, which could not be economically purified by distillation in a vacuum. Zinc dust (0·8 g.) was gradually added to a warm solution of the chloro-nitrile (2·5 g.) in alcohol (2 c.c.), acetic acid (1·2 c.c.), and water (1·5 c.c.) and the mixture was heated on the water-bath for ½ hour, filtered, concentrated, cooled, treated with dilute hydrochloric acid, and extracted with ether. Evaporation of the dried extracts left ethyl phenoxyacetate-2-acetonitrile as a pale yellow oil (1·8 g.), b. p. 201—203°/25 mm. On being refluxed with alcohol (50 c.c.) and sulphuric acid (25 c.c.) for 10 hours, this nitrile (10 g.) was converted into the ethyl phenoxyacetate-2-acetate (11·5 g.), m. p. and mixed m. p. 48—49° after crystallisation from light petroleum.

7-Hydroxychromeno-(3′ : 4′ : 4 : 3)-coumarin.—A solution of the foregoing ester (5 g.) in toluene (25 c.c.) was gradually added to powdered sodium (0·6 g.) in the same solvent (25 c.c.), and the mixture heated on the water-bath for 1½ hours, cooled, and treated with excess of 2% aqueous sodium hydroxide. The liquid was filtered to remove a small amount of solid, the toluene layer separated, and the alkaline liquor extracted with ether to remove remaining traces of toluene, and acidified with dilute hydrochloric acid. On isolation with ether, the resulting ethyl chroman-3-one-4-carboxylate was obtained as a pale yellow oil (1 g.), which gave a prussian-blue coloration with alcoholic ferric chloride. Acidification of an aqueous solution of the solid separating from the toluene–water mixture gave a further quantity (0·5 g.) of the ester.

From a solution of the ester (1 g.) and resorcinol (1 g.) in alcohol (10 c.c.) saturated with hydrogen chloride, the *coumarin* (0·2 g.) gradually separated in the course of 3 days; a further quantity (0·1 g.) was obtained by concentration of the alcoholic liquors. The substance crystallised from alcohol in pale yellow needles, m. p. 276—278° (Found: C, 72·3; H, 3·9. $C_{16}H_{10}O_4$ requires C, 72·2; H, 3·8%). The *acetate* formed slender, pale yellow prisms, m. p. 214—215°, from ethyl acetate (Found: C, 70·3; H, 4·1. $C_{18}H_{12}O_5$ requires C, 70·1; H, 3·9%).

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101. *Hydroxy-carbonyl Compounds. Part XI. Phosphoryl Chloride a a Condensing Agent.*

By (MISS) IVY GOODALL and ALEXANDER ROBERTSON.

IN the present work it has been found that with a series of esters of acylacetic acids th Simonis reaction applied to *p*-xylenol proceeds smoothly, giving small yields of 5 : 8-d methylchromones, but all attempts to effect similar condensations by the Pechman method were unsuccessful. The failure to obtain products by the latter procedure, whic normally produces coumarins, led us to explore the use of phosphoryl chloride, a reage which Naik and co-workers (*J. Indian Chem. Soc.*, 1929, **6**, 801) employed to prepa coumarins from ethyl α-benzylacetoacetate and resorcinol, phloroglucinol, pyrogallol, a α-naphthol. With this reagent, ethyl acetoacetate and *p*-xylenol formed an intractab ... ethyl α-methyl-, ethyl α-ethyl-, and ethyl α-benzyl-acetoacetate and ethyl benzo

acetate gave rise to chromones, identical with the respective specimens obtained by the phosphoric oxide method.

On extending this procedure to the condensation of the same series of esters with *m*-4-xylenol, which has been shown to yield chromones by the Simonis method (Part X; J., 1936, 215), it was found that, whereas ethyl acetoacetate gave rise to 4 : 6 : 8-trimethylcoumarin, ethyl α-methyl- and ethyl α-ethyl-acetoacetate yielded 2 : 3 : 6 : 8-tetramethyl- and 2 : 6 : 8-trimethyl-3-ethyl-chromone respectively; pyrones could not be isolated from the tars formed in the case of ethyl α-benzylacetoacetate and ethyl benzoylacetate.

These results, we believe, indicate that in the condensation of acylacetic esters with phenols by means of phosphoryl chloride the course of the reaction tends to follow closely that obtaining with phosphoric oxide. The exception observed in the condensation of ethyl acetoacetate with *m*-4-xylenol is not unexpected, as it has already been established that, compared with its analogues, this ester may behave abnormally in the Simonis reaction (J., 1932, 1180, 1681). Further, the results of Naik and co-workers (*loc. cit.*) are also in keeping with this view, because the phenols employed by these authors have been shown to give rise to coumarins invariably by the Simonis reaction (J., 1931, 1255, 1877, 2426).

Experimental.

2 : 5 : 8-*Trimethylchromone*.—A mixture of *p*-xylenol (10 g.) and ethyl acetoacetate (10 g.) was heated with phosphoric oxide (15 g.) for 1¾ hours; after 1 hour, more oxide (15 g.) was added. An aqueous digest of the cooled mixture was basified with sodium hydroxide and extracted with ether. The ethereal extracts were washed several times with 2% aqueous sodium hydroxide, dried, and evaporated, leaving the *product* as an oil which gradually solidified, and then separated from light petroleum in colourless rods, m. p. 81° (Found : C, 76·5; H, 6·4. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%). Condensation of this substance (0·5 g.) and piperonal (0·35 g.) in boiling alcohol (10 c.c.) with sodium ethoxide (from 0·06 g. of sodium) during 1 hour gave 2-(3′ : 4′-*methylenedioxystyryl*)-5 : 8-*dimethylchromone*, forming yellow needles from alcohol, m. p. 183° (Found : C, 74·8; H, 5·1. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

2 : 3 : 5 : 8-*Tetramethylchromone* separated from the phosphoric oxide reaction mixture which had been digested with water and basified; it crystallised from ether or light petroleum (b. p. 40—60°) in colourless plates, m. p. 96·5—97·5° (Found : C, 77·2; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%). Condensed with piperonal, it gave 2-(3′ : 4′-*methylenedioxystyryl*)-3 : 5 : 8-*trimethylchromone*, which separated from alcohol in yellow needles, m. p. 226° (Found : C, 75·7; H, 5·5. $C_{21}H_{18}O_4$ requires C, 75·4; H, 5·4%).

A mixture of *p*-xylenol (2 g.), ethyl α-methylacetoacetate (2 g.), and phosphoryl chloride (1 c.c.) was heated on the steam-bath for 2 hours, cooled, mixed with water, and basified with sodium hydroxide. Recrystallisation of the product from much boiling water and then light petroleum gave the chromone in plates, m. p. 98°, undepressed on admixture with an authentic specimen (Found : C, 77·3; H, 6·9%).

2 : 5 : 8-*Trimethyl-3-ethylchromone* was obtained with the aid of phosphoric oxide and on crystallisation from ether formed colourless elongated prisms, m. p. 86·5° (Found : C, 78·0; H, 7·6. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%). With piperonal it gave 2-(3′ : 4′-*methylenedioxystyryl*)-5 : 8-*dimethyl-3-ethylchromone*, which formed yellow needles from methyl alcohol, m. p. 153° (Found : C, 75·7; H, 5·7. $C_{22}H_{20}O_4$ requires C, 75·8; H, 5·8%).

The same chromone was obtained when phosphoryl chloride was used as condensing agent, m. p. and mixed m. p. 87° (Found : C, 78·0; H, 7·5%).

5 : 8-*Dimethylflavone*.—Condensation of *p*-xylenol (4 g.) with ethyl benzoylacetate (4·7 g.) by means of phosphoric oxide (15 g.) for periods varying from 15 minutes to 1½ hours gave rise to viscous, dark brown products. Slow evaporation of alcoholic solutions of this material deposited the *flavone*, which then separated readily from warm alcohol in pale yellow, elongated, flat prisms, m. p. 171°, identical with a specimen obtained from the cleaner reaction product formed by the phosphoryl chloride method (Found : C, 81·5; H, 5·6. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

3-*Benzyl*-2 : 5 : 8-*trimethylchromone*.—(A) Condensation of *p*-xylenol and ethyl α-benzylacetoacetate with phosphoric oxide in the usual manner, followed by treatment of the reaction mixture with excess water and then sodium hydroxide, gave rise to a semi-solid, which was isolated with ether. On cooling, a solution of this material in a small volume of warm alcohol deposited a compound (X) in colourless prismatic needles, m. p. 93° after repeated crystallisation

from alcohol (Found : C, 76·9; H, 6·7%). This compound, which failed to give a styryl derivative with piperonal under the usual conditions, does not appear to be a coumarin and, although it is insoluble in water and 8% aqueous sodium hydroxide, is not precipitated from an alcoholic solution by the latter reagent.

Evaporation of the alcoholic residues from the crude compound (X) left oily material, which was shown to contain the chromone, since on warming with alcoholic sodium ethoxide and piperonal it gave 2-(3′ : 4′-*methylenedioxystyryl*)-3-*benzyl*-5 : 8-*dimethylchromone*, forming sparingly soluble, yellow needles, m. p. 222°, from acetic acid or acetic acid–alcohol (Found : C, 79·3; H, 5·6. $C_{27}H_{22}O_4$ requires C, 79·0; H, 5·4%).

(B) Condensation of *p*-xylenol (10 g.) with ethyl α-benzylacetoacetate (10 g.) in the presence of phosphoryl chloride (5 g.) on the water-bath for 4 hours gave rise to a cleaner reaction product than is produced by method (A). From this material the substance (X), m. p. 93°, was isolated as before. The alcoholic mother-liquors left on removal of (X) were mixed with excess of 8% aqueous sodium hydroxide and the resulting precipitate was collected, dissolved in a little alcohol and reprecipitated in the same manner. The product thus obtained consisted mainly of 3-*benzyl*-2 : 5 : 8-*trimethylchromone*, which was purified by repeated crystallisation from a small volume of methyl alcohol, forming colourless prismatic needles, m. p. 101° (Found : C, 82·0; H, 6·5. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%). On condensation with piperonal this compound gave an almost theoretical yield of the styryl derivative, m. p. and mixed m. p. 222°, after crystallisation from alcohol–acetic acid.

4 : 6 : 8-*Trimethylcoumarin*.—The dark blue mixture produced by heating *m*-4-xylenol (2 g.), ethyl acetoacetate (2 g.) and phosphoryl chloride (1 g.) for 3 hours was mixed with excess of water, and the solution basified. Crystallisation of the resulting solid from light petroleum (b. p. 40—60°) gave material, m. p. 108—109°, from which 4 : 6 : 8-trimethylcoumarin was obtained by repeated crystallisation from dilute alcohol, m. p. 113—114°, undepressed by admixture with an authentic specimen, m. p. 114° (Part X, *loc. cit.*) (Found : C, 76·4; H, 6·4%). It is not unlikely that this coumarin was accompanied by traces of the isomeric chromone.

When ethyl acetoacetate was replaced by ethyl α-methylacetoacetate in the above reaction, 2 : 3 : 6 : 8-tetramethylchromone was obtained, m. p. 135—136° (Found : C, 76·9; H, 7·1%). Similarly, ethyl α-ethylacetoacetate gave 2 : 6 : 8-trimethyl-3-ethylchromone, m. p. 112° (Found : C, 77·7; H, 7·5%). Both chromones were identified by comparison with authentic specimens (Part X, *loc. cit.*).

University of Liverpool. [*Received, March 9th, 1936.*]

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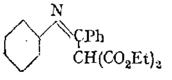
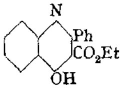
102. *Imidochlorides. Part III. Reaction of Anilide Imidochlorides and Ethyl Sodiomalonate.*

By R. C. Shah and V. R. Heeramaneck.

Just condensed benzanilide imidochloride with ethyl sodiomalonate in ether and obtained ethyl mono- and di-(phenyliminobenzyl)malonate, the former (I) of which underwent ring closure on heating to give ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate (II) (*Ber.*, 1885, **18**, 2623, 2632; 1886, **19**, 979, 1541; see also Seka and Feuchs, *Monatsh.*, 1931, **57**, 52).

(I.) 

 (II.)

A substantial improvement of the method is the use of toluene as solvent and of ethyl malonate (1 mol.) together with its sodio-derivative (1 mol.), which minimises the formation of the dicondensation product. Crystalline monocondensation products have thus been obtained in good yields from various anilide imidochlorides, and cyclised to the corresponding quinolines, the yields of which are 30—40%, calculated on the imidochloride employed. The presence of substituents does not appear to influence appreciably the condensation or the cyclisation.

Cyclisation of (I) has also been effected by (i) phosphoryl chloride, which gives the carbethoxyquinoline, and (ii) concentrated sulphuric acid, which affords the quinoline-carboxylic acid.

The action of *p*-toluidine on (I) produces *(phenyliminobenzyl)malonodi*-p-*toluidide* at 110—120° and the p-*toluidide* of 4-hydroxy-2-phenylquinoline-3-carboxylic acid at 150°. Benzoylation of the sodium derivative of (I) affords *ethyl benzoyl(phenyliminobenzyl)-malonate*, which is not cyclised by heating.

The condensation product obtained from benzo-*m*-toluidide imidochloride gives on ring closure a mixture of *ethyl 4-hydroxy-2-phenyl-5-* and *-7-methylquinoline-3-carboxylate*, which are separable by fractional crystallisation.

Experimental.

Reaction of Benzanilide Imidochloride with Ethyl Sodiomalonate.—By Just's method, benzanilide imidochloride (10 g.) gave 2 g. of the monocondensation product, m. p. 75°, and 2 g. of the dicondensation product, m. p. 160°.

A solution of benzanilide imidochloride (150 g.; 1 mol.) in dry toluene was refluxed for 2 hours with a mixture of ethyl sodiomalonate (1 mol.), ethyl malonate (112 g.; 1 mol.), and toluene, and the whole mixed with water. The product extracted by ether was heated at 120—125°/30—40 mm. to remove toluene and the excess of malonic ester; the residual oil solidified at 0° and on crystallisation from alcohol gave 85 g. (38%) of ethyl (phenyliminobenzyl)malonate (I), m. p. 75°. No dicondensation product could be isolated. The product (I) was quantitatively converted at 150—170° into ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate (II), m. p. 258—260° (Just, m. p. 260°) (yield 38%, calculated on the imidochloride employed), which was hydrolysed with aqueous-alcoholic sodium hydroxide to the carboxylic acid, m. p. 230—232° (Just, m. p. 232°).

Cyclisation of Ethyl (Phenyliminobenzyl)malonate (I) by Phosphoryl Chloride and by Sulphuric Acid.—(i) A mixture of (I) (2 g.) and phosphoryl chloride (16 c.c.) was refluxed for 1 hour, cooled, and poured on ice. The solid was washed with cold alcohol and crystallised from nitrobenzene, yielding 1·2 g. of (II), m. p. and mixed m. p. 259—260°. (ii) The compound (I) (2 g.) was mixed with concentrated sulphuric acid (8 c.c.) and kept at room temperature for a few days until a test portion gave an immediate white precipitate with water; the whole was then diluted with water. The precipitated acid crystallised from alcohol in colourless needles, m. p. and mixed m. p. with the carboxylic acid described above, 229—231°.

Action of p-*Toluidine on Ethyl (Phenyliminobenzyl)malonate (I).*—(i) The ester (0·5 g.) and *p*-toluidine (0·4 g.) were heated together at 110—120° for 4 hours and the cooled melt was treated with dilute hydrochloric acid. The oil obtained solidified (0·2 g.) and then crystallised from alcohol in needles of *(phenyliminobenzyl)malonodi*-p-*toluidide*, m. p. 208—210° (Found: N, 9·3. $C_{30}H_{27}O_2N_3$ requires N, 9·1%), soluble in hot methyl and ethyl alcohol and insoluble in hot chloroform and benzene. (ii) When the reaction was carried out at 150°, the product was the p-*toluidide of 4-hydroxy-2-phenylquinoline-3-carboxylic acid*, crystallising from alcohol in needles, m. p. 255—257° (Found: N, 7·8. $C_{23}H_{18}O_2N_2$ requires N, 7·9%), and obtainable also from (II) and *p*-toluidine at 190—200° after 4 hours' heating.

Ethyl Benzoyl(phenyliminobenzyl)malonate.—An ethereal solution of (I) (5 g.) was slowly added to a mixture of pulverised sodium (0·5 g.) and dry ether, followed by a small excess of benzoyl chloride, the mixture refluxed for 2 hours, and dilute sodium hydroxide solution added. The *product* extracted by ether crystallised from benzene–light petroleum in colourless needles (3·5 g.), m. p. 156—158° (Found: N, 3·4. $C_{27}H_{25}O_5N$ requires N, 3·2%).

The following compounds were prepared by the methods described above and cyclisation was effected by heating, usually at 180—190°. The condensation products are easily soluble in common organic solvents, whereas the carbethoxyquinolines are only sparingly soluble; they were mostly crystallised from alcohol. The yields of the condensation products and quinolines given in parentheses are calculated on the imidochloride employed. By heating at a high temperature the mother-liquor from which the condensation product has been separated, a further small quantity of the quinoline can be obtained.

*Ethyl (phenylimino-*p-*nitrobenzyl)malonate* (45%), large, hard, monoclinic, highly refractive, yellow crystals with a blue fluorescence, m. p. 101° (Found: N, 7·2. $C_{20}H_{20}O_6N_2$ requires N, 7·3%); *ethyl 4-hydroxy-2-(*p-*nitrophenyl)quinoline-3-carboxylate* (38%), tiny, pale yellow needles, m. p. 239—241° (Found: N, 8·0. $C_{18}H_{14}O_5N_2$ requires N, 8·3%); the *carboxylic acid*,

needles (from acetic acid), m. p. 197—199° (efferv.) (Found: N, 9·5. $C_{16}H_{10}O_5N_2$ requires N, 9·0%).

Ethyl (phenylimino-o-chlorobenzyl)malonate (45%), monoclinic colourless crystals, m. p. 77° (Found: Cl, 9·3. $C_{20}H_{20}O_4NCl$ requires Cl, 9·5%); *ethyl 4-hydroxy-2-o-chlorophenylquinoline-3-carboxylate* (40%), colourless needles, m. p. 239—242° (Found: Cl, 11·2. $C_{18}H_{14}O_3NCl$ requires Cl, 10·8%); the *carboxylic acid*, colourless needles, m. p. 242—244° (Found: Cl, 12·2. $C_{16}H_{10}O_3NCl$ requires Cl, 11·9%). *Ethyl (p-nitrophenyliminobenzyl)malonate* (40%), lemon-yellow monoclinic crystals with a blue fluorescence, m. p. 103° (Found: N, 7·7. $C_{20}H_{20}O_6N_2$ requires N, 7·3%); *ethyl 6-nitro-4-hydroxy-2-phenylquinoline-3-carboxylate* (35%), light feathery crystals, m. p. above 300° (Found: N, 7·8. $C_{18}H_{14}O_5N_2$ requires N, 8·3%); the *carboxylic acid*, pale yellow needles (from acetic acid), m. p. 295—297° (Found: N, 9·2. $C_{16}H_{10}O_5N_2$ requires N, 9·0%). Ethyl (*o*-tolyliminobenzyl)malonate (35%), monoclinic crystals, m. p. 95° (Found: N, 4·1. Calc. for $C_{21}H_{23}O_4N$: N, 4·0%) (Just, *Ber.*, 1886, **19**, 1541, gives m. p. 95°); ethyl 4-hydroxy-2-phenyl-8-methylquinoline-3-carboxylate (30%), colourless needles, m. p. 242° (Found: N, 4·8. Calc. for $C_{19}H_{17}O_3N$: N, 4·6%) (Just, *loc. cit.*, gives m. p. 208·5°); the *carboxylic acid*, m. p. 201—203° (decomp.) (Found: N, 5·2. $C_{17}H_{13}O_3N$ requires N, 5·0%). *Ethyl (m-tolyliminobenzyl)malonate* (45%), colourless needles, m. p. 67—68° (Found: N, 4·2%); when heated, it gave a mixture (40%), m. p. 189—240°, separated by five crystallisations from ethyl acetate into sparingly soluble *ethyl 4-hydroxy-2-phenyl-(5 or 7)-methylquinoline-3-carboxylate*, m. p. 237—240° (Found: N, 4·6. $C_{19}H_{17}O_3N$ requires N, 4·6%), and easily soluble *ethyl 4-hydroxy-2-phenyl-(7 or 5)-methylquinoline-3-carboxylate*, m. p. 225—228° (Found: N, 4·8%); mixed m. p. 195—240°. *Ethyl (p-tolyliminobenzyl)malonate* (30%), colourless needles, m. p. 62—63° (described as a viscid oil by Just, *Ber.*, 1886, **19**, 979) (Found: N, 4·3%); ethyl 4-hydroxy-2-phenyl-6-methylquinoline-3-carboxylate (29%), m. p. 253—254° (Just gives m. p. 236°) (Found: N, 5·0. Calc. for $C_{19}H_{17}O_3N$: N, 4·6%); the *carboxylic acid*, needles, m. p. 209—211° (decomp.) (Found: N, 5·1. $C_{17}H_{13}O_3N$ requires N, 5·0%).

Benzo-o-chloroanilide imidochloride, prepared from benzo-*o*-chloroanilide (40 g.) and phosphorus pentachloride (41 g.), distilled at 214—215°/40 mm. Yield, 33 g. (Found: N, 5·5. $C_{13}H_9NCl_2$ requires N, 5·6%). It is easily soluble in all the common organic solvents. It was characterised by its amidine, prepared by Shah's modified method (*J. Indian Inst. Sci.*, 1925, **7**, 219). Aniline (2 g.) was slowly added to a mixture of freshly distilled diethylaniline (6 g.) and the imidochloride (2 g.), and the whole heated on the water-bath for 1 hour. Treatment with dilute hydrochloric acid gave the sparingly soluble hydrochloride, which on trituration with aqueous ammonia and alcohol gave *o'-chlorodiphenylbenzamidine*, which crystallised from alcohol in colourless needles, m. p. 113—114° (Found: Cl, 11·3. $C_{19}H_{15}N_2Cl$ requires Cl, 11·6%). The *hydrochloride*, obtained from the amidine and concentrated hydrochloric acid in glacial acetic acid, had m. p. 219—220° (Found: Cl, 20·8. $C_{19}H_{15}N_2Cl,HCl$ requires Cl, 20·7%). *Ethyl (o-chlorophenyliminobenzyl)malonate* (40%) formed colourless needles, m. p. 104—105° (Found: Cl, 9·7. $C_{20}H_{20}O_4NCl$ requires Cl, 9·5%), *ethyl 8-chloro-4-hydroxy-2-phenylquinoline-3-carboxylate* (32%) had m. p. 155—156° (Found: Cl, 11·0. $C_{18}H_{14}O_3NCl$ requires Cl, 10·8%), and the *carboxylic acid* m. p. 184—186° (Found: Cl, 11·8. $C_{16}H_{10}O_3NCl$ requires Cl, 11·9%).

Benzo-m-chloroanilide imidochloride, obtained from benzo-*m*-chloroanilide (45 g.) and phosphorus pentachloride (43 g.), distilled at 229—231°/50 mm. Yield, 35 g. (Found: N, 5·6%). *m-Chlorodiphenylbenzamidine* crystallised from alcohol in needles, m. p. 123—124° (Found: Cl, 11·3%), and its *hydrochloride* had m. p. 233—235° (Found: Cl, 20·6%). Ethyl (*m*-chlorophenyliminobenzyl)malonate, a viscous oil, on heating gave a product, m. p. 180—220°, from which, by fractional crystallisation from ethyl acetate, *ethyl (5 or 7)-chloro-4-hydroxy-2-phenylquinoline-3-carboxylate*, m. p. 234—237°, was isolated (Found: Cl, 10·5. $C_{18}H_{14}O_3NCl$ requires Cl, 10·8%).

Ethyl (p-chlorophenyliminobenzyl)malonate (35%) melted at 75° (Found: Cl, 9·5%), *ethyl 6-chloro-4-hydroxy-2-phenylquinoline-3-carboxylate* (30%) at 251—252° (Found: Cl, 11·1%), and the *carboxylic acid* at 300° (Found: Cl, 11·6%).

The work is being extended to the condensation of anilide imidochlorides with β-diketones and β-ketonic esters.

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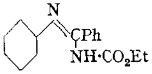
Royal Institute of Science, Bombay. [*Received, November 18th, 1935.*]

103. *Imidochlorides. Part IV. Condensation of Anilide Imidochlorides with Urethanes. A New Synthesis of 4-Hydroxy-2-phenylquinazolines.*

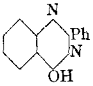
By R. C. Shah and M. B. Ichaporia.

There are but few recorded observations on the synthesis of heterocyclic nitrogen compounds from anilide imidochlorides (see Just, *Ber.*, 1885, **18**, 2623, 2632; 1909, **42**, 3360; preceding paper). The formation of 3-chloro-4-anilino-2-chloromethylquinolines from chloroacetanilides and phosphorus pentachloride takes place through the intermediately formed imidochlorides (*Ber.*, 1930, **63**, 3191).

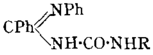
As part of a comprehensive study of the problem, we have investigated the condensation of anilide imidochlorides with urethanes. The direct condensation of benzanilide imidochloride and urethane is a complex reaction, but a smooth condensation took place when the sodium derivative of urethane was used. The product, *(phenyliminobenzyl)urethane* (I), was feebly basic and formed a crystalline hydrochloride. As amidines of this type are not known, its characteristic reactions were examined. The action of heat led to 4-hydroxy-2-phenylquinazoline (II) (Bischler and Lang, *Ber.*, 1895, **28**, 289; Bhattacharya, Bose, and Ray, *J. Indian Chem. Soc.*, 1929, **6**, 286), the constitution of (I) being thus confirmed. The amidine (I) was easily decomposed by hydrolysis with the formation of benzanilide. The action of bromine gave benzo-*p*-bromoanilide, probably through the dibromo-additive product initially formed (cf. Hantzsch, *Ber.*, 1890, **23**, 2774). The action of α- and β-naphthylamine afforded crystalline *ureas* (III, R = α- or β-naphthyl).



(I.)



(II.)



(III.)

Benzanilide imidochloride condensed similarly with methyl carbamate and with acetylurethane. *Acetyl(phenyliminobenzyl)urethane*, a crystalline solid, was cyclised by heating to *3-acetyl-2-phenyl-4-quinazolone*, which could not be obtained by acetylation of (II).

Benzo-α- and -β-naphthalide imidochlorides on condensation with urethane yielded (α- and β-*naphthyliminobenzyl)urethanes*, which underwent cyclisation on heating, giving *4-hydroxy-2-phenyl-*1 : 3-*naphtha*iso*diazine* and 1-*hydroxy-*3-*phenyl-*2 : 4-*naphtha*iso*diazine* respectively; the ring closure in the latter case is assumed to take place in the α-position with the production of the angular compound (cf. Lindner and Staufer, *Monatsh.*, 1925, **46**, 231).

Experimental.

Condensation of Benzanilide Imidochloride with Urethane.—A mixture of pulverised sodium (1 g., 1 atom.) and dry ether (80 c.c.) was treated with a solution of urethane (12·2 g., 3 mols.) in dry ether (80 c.c.), added drop by drop, and the whole was kept over-night, the sodium compound separating, and then refluxed for 12 hours with an ethereal solution of benzanilide imidochloride (10 g., 1 mol.). Water was added, and benzanilide (1·5 g.) removed by filtration. The residue obtained from the ethereal solution was washed with water, redissolved in ether (benzanilide separated), dried, and recovered as a turbid yellow oil containing a trace of benzanilide. By repeated solution in warm light petroleum (b. p. 60—70°) and recovery, *(phenyliminobenzyl)urethane* (I) was obtained as a clear yellow, viscous oil (8 g.), which could not be distilled without conversion into the quinazoline. For analysis, it was purified through the hydrochloride (Found: C, 71·0; H, 6·3; N, 9·7. $C_{16}H_{16}O_2N_2$ requires C, 71·7; H, 6·0; N, 10·4%). The *hydrochloride* separated in colourless needles, m. p. 215—217°, on addition of dry ether to a solution of the substance in methyl-alcoholic hydrogen chloride (Found: Cl, 11·9. $C_{16}H_{16}O_2N_2$,HCl requires Cl, 11·7%).

Reactions of (Phenyliminobenzyl)urethane.—(1) By 2 hours' heating at 180—190°, the urethane (2 g.) was converted into 4-hydroxy-2-phenylquinazoline, which crystallised from alcohol in colourless needles (0·6 g.), m. p. 230—232° (Found: N, 12·7. Calc. for $C_{14}H_{10}ON_2$: N, 12·6%)

undepressed by a specimen prepared by the method of Bhattacharya, Bose, and Ray (*loc. cit.*), who give m. p. 222—223°.

(2) The urethane (2 g.), heated with water (20 c.c.) at 140—150° for 5 hours or with concentrated hydrochloric acid (10 c.c.) at 70—80° for ½ hour, gave benzanilide, m. p. 158—160° after crystallisation from alcohol.

(3) Bromine (0·6 g.) and the urethane (1 g.) in chloroform gave benzo-*p*-bromoanilide, m. p. (after crystallisation from alcohol) and mixed m. p. 202—203° (Found : Br, 29·4. Calc. : Br, 29·0%).

(4) A mixture of the urethane (2 g.) and α-naphthylamine (1·5 mols.) was heated at 100—110° for 4 hours; the product solidified on cooling, and on crystallisation from boiling alcohol gave colourless needles of s.-(*phenyliminobenzyl*)-α-*naphthylurea* (III, R = α-naphthyl), m. p. 258—260° (Found : N, 11·4. $C_{24}H_{19}ON_3$ requires N, 11·5%). The corresponding β-naphthylamine *derivative* had m. p. 273—278° (Found : N, 11·3%).

Methyl (Phenyliminobenzyl)carbamate.—When methyl carbamate was substituted for urethane in the above condensation, the product was *methyl (phenyliminobenzyl)carbamate*, a yellow oil easily soluble in the common organic solvents (Found : N, 10·5. $C_{15}H_{14}O_2N_2$ requires N, 11·0%). The action of heat, hydrolysis, the action of α-naphthylamine, and bromination gave products identical with those obtained from (I).

Acetyl(phenyliminobenzyl)urethane.—This *compound* (7 g.), obtained from acetylurethane (18 g.), pulverised sodium (1·6 g.), and benzanilide imidochloride (10 g.) by the procedure described for the condensation with urethane, solidified after long standing and then crystallised from alcohol in fine colourless needles, m. p. 85—88° (Found : C, 69·2; H, 6·1; N, 9·4. $C_{18}H_{18}O_3N_2$ requires C, 69·7; H, 5·8; N, 9·0%).

3-*Acetyl-2-phenyl-4-quinazolone.*—The foregoing compound was heated at 210—220° for 1 hour. The reddish-brown viscous product solidified when washed with cold alcohol and then crystallised from hot alcohol in pale yellow needles of the *quinazolone*, m. p. 233°, depressed by (II) (Found : N, 10·3. $C_{16}H_{12}O_2N_2$ requires N, 10·6%).

(α-*Naphthyliminobenzyl)urethane.*—Benzo-α-naphthalide imidochloride (Just, *Ber.*, 1886, **19**, 984) (22 g.) on condensation with the sodium derivative of urethane by the usual method gave (α-*naphthyliminobenzyl)urethane* (15 g.) as a yellow viscous oil (Found : N, 8·8. $C_{20}H_{18}O_2N_2$ requires N, 8·8%). Cyclisation by heating at 200—205° for 2 hours gave 4-*hydroxy-2-phenyl*-1 : 3-*naphthaisodiazine* which crystallised from alcohol in colourless needles, m. p. 300° (Found : N, 10·0. $C_{18}H_{12}ON_2$ requires N, 10·3%).

(β-*Naphthyliminobenzyl)urethane*, prepared from benzo-β-naphthalide imidochloride (Just, *loc. cit.*) (15 g.), was obtained as a yellow oil (8 g.) (Found : N, 9·0%). Heated at 190° for 1½ hours, it gave 1-*hydroxy-3-phenyl*-2 : 4-*naphthaisodiazine*, which formed colourless prismatic needles, m. p. 295—298°, from alcohol (Found : N, 10·0%).

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104. *The Mechanism of Additions to Double Bonds. Part III. Molecular Forces between Benzoquinone and* cyclo*Pentadiene.*

By Albert Wassermann.

London has given the following approximation formula for the attraction energy for simple molecules due to the "dispersion effect" (*Z. Physik*, 1930, **63**, 243; *Z. physikal. Chem.*, 1930, **11**, *B*, 222) :

$$\varepsilon_{kl} = \frac{3}{2} \times \frac{P_k P_l}{R^6} \frac{\Delta E_k \times \Delta E_l}{\Delta E_k + \Delta E_l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R is the distance between the molecules k and l. The polarisability P of these molecules at the frequency ν is given by

$$P_k(\nu) = \frac{1}{m}\left(\frac{eh}{2\pi}\right)^2 \sum_{k'} \frac{f_{kk'}}{(E_{k'} - E_k)^2 - h^2\nu^2}$$

and similarly for $P_l(\nu)$; here m is the mass of the electron and $f_{kk'}$ the oscillator strength ("number of dispersion electrons") corresponding to the eigenfrequency $(E_{k'} - E_k)/h$.

The energy difference corresponding to the greatest f value is termed ΔE_k. In this communication an attempt is made to extend the use of formula (1) to the calculation of energies between large organic molecules. Such an attempt is not in contradiction with the assumptions under which formula (1) has been deduced. The attraction between each bond in k and each bond in l is separately calculated and then added together to give the total dispersion effect, additivity being a characteristic property of these molecular forces. The approximately constant bond refractivities, which, it is known, can be ascribed to the various bonds in organic molecules (cf. Smyth, *Phil. Mag.*, 1925, **50**, 301; Fajans aud Knorr, *Ber.*, 1926, **59**, 245), can be used for the calculation of P in formula (1). The polarisabilities here involved have been regarded as isotropic spheres located in a point in the middle of each bond (cf. also p. 435); R in (1) is the distance between these points in k and l respectively. It has been observed in many cases that some bonds (*e.g.*, conjugated double bonds) have not only a characteristic refractivity but also a characteristic absorption from which ΔE_k and ΔE_l can be estimated. As no absorption bands of C—C or C—H bonds are known,* the ionisation energy of carbon (11 e.v.) has been used for ΔE_{C-C}, and half the sum of the ionisation energy of carbon and hydrogen (12 e.v.) for ΔE_{C-H}.†

If the application of formula (1) is permissihle in the case of large molecules, and if the order of magnitude of the ΔE values has been correctly estimated, then the calculated lattice energy of organic crystals should be of the same order of magnitude as the experimentally determined heat of sublimation. This has been proved to be true for the case of benzoquinone (see Section 1). In Parts I and II (J., 1935, 828, 1511) the dipole induction energies for different mutual orientations of benzoquinone and *cyclo*pentadiene were calculated, and it was shown that, under certain assumptions, the difference in the induction energies was sufficient to explain the actual course of the additive reaction. One of the assumptions concerns the magnitude of the dispersion effect. In Section 2, values of this dispersion effect are calculated and compared with the dipole induction energies.

1. *The Lattice Energy of Benzoquinone.*—The mutual orientation of the molecules in the benzoquinone crystal is known (Robertson, *Proc. Roy. Soc.*, 1935, **150**, 106). For the C—H distance the value (*viz.*, 1·1 Å.) given in Part I (Figs. 2—4) was used. The P and ΔE values are given below.

Bond	C=C (Benzoquinone).	C=O (Benzoquinone).	C—C.	C—H.
$P \times 10^{24}$ (cm.^{3})	1·87	1·58	0·478	0·671
ΔE (e.v.)	5·2	5·2	11	12

The " non-localised " electrons in the conjugated double bonds of benzoquinone produce a certain exaltation of the molecular refractivity (cf. von Auwers, *Ber.*, 1927, **60**, 2143); this exaltation was regarded as being equally distributed between the four double bonds. The refraction of the C=C bond is then 4·75, and that of the C=O bond 4·02; from these figures the P values quoted above were calculated. The ΔE value for the C=C and the C=O bond was deduced from an absorption band at 2400 Å. in benzoquinone vapour ‡ (Light, *Z. physikal. Chem.*, 1926, **122**, 414). That this band does really correspond to an excitation of electrons of the conjugated double bonds is rendered very probable by a comparison with the absorption spectra of the polyenes (cf. Hausser, Kuhn, *et al.*, *Z. physikal. Chem.*, 1935, **29**, *B*, 363). The observed regular displacement of the position and intensities of the bands of the polyenes as the number of double bonds is increased indicates that the electrons of conjugated double bonds are so closely coupled that for many purposes they can be treated collectively. It is therefore also justifiable to attach only one ΔE

* The deduction of ΔE values for C—C and C—H bonds from magnetic susceptibilities is possible (private communications from Dr. Eisenschitz and Dr. Muller; cf. a paper in *Proc. Roy. Soc.* in press).

† The same ΔE values have been used by Muller in calculating the heats of sublimation of some aliphatic hydrocarbons (preliminary communication in " The Solid State of Matter," International Congress of Physics, 1934, **2**, 52). The second ionisation potential of benzene is 11·7 ± 0·3 e.v. (Price and Wood, *J. Chem. Physics*, 1935, **3**, 439). This value is almost the same as that used for ΔE_{C-H}.

‡ This band is also shown by solutions; its f value is about 1000 times as great as that of the band to which the yellow colour of quinone is due.

value to each system of conjugated double bonds of other compounds, *e.g.*, benzoquinone or *cyclo*pentadiene. These values are, of course, considerably smaller than the minimum ΔE value of ethylene (for the absorption of ethylene, cf. Scheibe and Grieneisen, *Z. physikal. Chem.*, 1934, **25**, *B*, 52).

The figure shows a part of the benzoquinone lattice. The energy between molecule 1 and a number of other molecules is given in Table I.

TABLE I.

Energies (ergs $\times\ 10^{14}$*) between various molecules in the benzoquinone lattice.*

Molecules (see fig.)	1—2	1—3	1—4	1—5	1—6	1—7
Dispersion effect	−15	− 4	− 1·0	− 5·7	− 1·8	− 5·0
Dipole-induction energy	− 6	− 1·3	− 0·5	− 1·4	− 0·2	− 2·0
Dipole energy	− 9	− 8·6	− 1·0	+ 1·2	− 2·4	+ 9·6
Sum	−30	−13·9	− 2·5	− 5·9	− 4·4	+ 2·6

Calculation of the dispersion effect between the nearest C=C bonds of the molecules 1 and 2 gives

$$\varepsilon_{C=C(1),\,C=C(2)} = \frac{3 \times (1{\cdot}87 \times 10^{-24})^2 \times 5{\cdot}2^2 \times 4{\cdot}77 \times 10^{-10}}{2 \times R^6\,(5{\cdot}2 + 5{\cdot}2) \times 300}\ \text{erg}$$

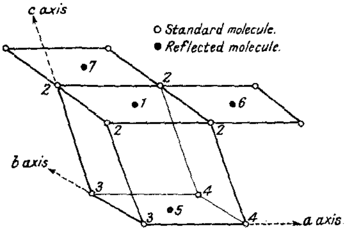
The distance R is 3·9 Å. (cf., *e.g.*, Fig. 4 in Robertson's paper). Each dispersion effect of Table I is the sum of 144 similarly calculated energies.

The dipole-induction energy was calculated as in Part I (*loc. cit.*). The dipole energy equals μF. F is the electric intensity (for calculation, see Part I) due to the two dipoles of k at the points at which one of the dipoles of l is regarded as localised; μ is the component of this dipole in the direction of F.

The lattice energy is obtained from the data of Table I as follows :

$$\tfrac{1}{2} \times 6{\cdot}06 \times 10^{23} \times 0{\cdot}239 \times 10^{-7} \times 10^{-14} \times 10^{-3} \times [4 \times 30 + 4 \times 13{\cdot}9 + 4 \times 2{\cdot}5 + 2 \times 5{\cdot}9 + 2 \times 4{\cdot}4 - 2 \times 2{\cdot}6] = 14{\cdot}6\ \text{kg.-cals./mol.} \quad (2)$$

The energy between molecule 1 and those molecules of the lattice which have not been included in the summation is only a few units per cent. of the total energy, and can be neglected.



Part of the benzoquinone lattice. The circles indicate the position of the centre of symmetry of the molecules. The mutual orientation of the molecules is shown in Robertson's paper (loc. cit.).

If the energy (2) is to be compared with the experimental heat of sublimation of benzoquinone, the kinetic energy of the crystal and the repulsive forces between the molecules should be taken into account. As a first approximation it seems justifiable to neglect these two terms (the repulsive forces were also neglected in London's calculation of lattice energies, *loc. cit.*) ; then the lattice energy, as calculated by (2), and the heat of sublimation should roughly coincide. This is the case, for the heat of sublimation (determined between − 7° and + 5° by Coolidge and Coolidge, *J. Amer. Chem. Soc.*, 1927, **49**, 105) is 15 kg.-cals./mol.* It can therefore be concluded that application of formula (1) is permissible, and that the order of magnitude of the ΔE values has been correctly estimated. If, as a second approximation, the repulsive forces are considered, then it is obvious that the calculated potential energy should be larger than 15 kg.-cals. As this was not found to be the case, it is probable that certain ΔE values are too small. The ΔE's of the double bonds were deduced from

* Such close agreement with the calculated figure is, of course, fortuitous.

experimentally observed absorption bands. On the other hand, the values of ΔE_{C-C} and ΔE_{C-H} were arbitrarily chosen, and it is therefore probable that these values are larger than 11 and 12 volts respectively.

A calculation of the lattice energy of benzoquinone, based only on the attraction due to the dipole and dipole-induction energy (cols. 3 and 4 of Table I) would give a value of 7 kg.-cals./mol. In spite of the fact that benzoquinone contains both the strongly polar C=O group and strongly polarisable double bonds, the classical dipole and dipole-induction energy does not amount to more than about 50%, at the most, of the total attraction.

2. *Dispersion Effect between Benzoquinone and* cyclo*Pentadiene.*—For the calculation of the data in Table III, the bond refractivities of *cyclo*pentadiene, as given in Part I, were used.* For the C=C bonds in *cyclo*pentadiene, a ΔE value of 6·2 e.v. was taken, corresponding to an absorption band in gaseous *cyclo*pentadiene at about 2000 Å. (Scheibe and Grieneisen, *loc. cit.*). Ethane absorbs continuously down to λ 1590 Å. It follows that in ethane, and certainly also in other molecules, ΔE_{C-C} and ΔE_{C-H} must be larger than 8 e.v.† Hence for ΔE_{C-C} and ΔE_{C-H}, not only the values taken before, but also a value of 8 e.v. was used. Those figures in Table III given in parentheses were calculated on the assumption that P_{C-H} is localised, not in the middle of each bond, but at a distance of 0·4 Å. from the centre of the carbon atom.

The mutual orientations of benzoquinone and *cyclo*pentadiene referred to are shown in Figs. 2—4 of Part I. The atomic distance d characterising the degree of separation of the two molecules is defined in the same way as before. From the data in Table II it can be seen that the closest packing between the carbon atoms of *cyclo*pentadiene and the carbon and oxygen atoms of benzoquinone corresponds to the intermediate configuration leading to the *endo*-1 : 4-addition product.

TABLE II.

Distance between carbon and oxygen atoms in different mutual orientations (intermediate configurations) of benzoquinone and cyclo*pentadiene.*

(Distance d arbitrarily chosen as 2·33 Å.)

		Intermediate configuration suitable for		
	α.	1 : 2-addition (cf. Fig. 4, Part I).	*exo*-1 : 4-addition (cf. Fig. 3, Parts I and II).	*endo*-1 : 4-addition (cf. Fig. 2, Parts I and II).
Number of carbon atoms of *cyclo*pentadiene which are at a distance of not more than α Å. from carbon atoms of benzoquinone	2·33	2	2	2
	2·4	2	2	4
	2·5	2	3	5
	β.			
Number of carbon atoms of *cyclo*pentadiene which are at a distance of not more than β Å. from oxygen atoms of benzoquinone	3·1	0	2	4
	3·5	2	3	4

As formula (1) is valid only when P/R^3 is considerably smaller than unity, the dispersion effect—in contrast to the dipole-induction energies as given in Parts I and II—cannot be calculated for d values smaller than about 2·33 Å. For $d = 2·33$ Å., $P/R^3 = 0·13$ at the most.

TABLE III.

Attraction energy (due to dispersion effect) between benzoquinone and cyclo*pentadiene in kg.-cals./mol.*; $d = 2·33$ Å.

ΔE_{C-C} and ΔE_{C-H}, e.v., used for calcn. of dispersion effect.	Intermediate configuration suitable for 1 : 2-addition.	*exo*-1 : 4-addition.	*endo*-1 : 4-addition.
8	−16·1	−21·9	−25·1
11 and 12	−19·0	−24·9 (−24·0)	−29·2 (−30·0)

1 : 2- *and* endo-1 : 4-*Addition.* The values in cols. 2 and 4 of Table III show that the dispersion effect is greater by 9—10 kg.-cals. when the molecules take up the orientation

* The fact that the calculated molecular refractivity of *cyclo*pentadiene is a little higher than the observed value (von Auwers, *Ber.*, 1912, **45**, 3077) was not taken into account.

† This conclusion is independent of the consideration discussed on p. 434.

suitable for *endo*-1 : 4-addition. Moreover, for this orientation, in which the carbon and oxygen atoms of the reacting molecules are more closely packed, the dipole-induction energy was found to be larger.

exo- *and* endo-*Addition*. In view of the closer packing of the carbon and oxygen atoms in the "*endo*-intermediate configuration," it would be expected *a priori* that here the dispersion effect would be larger. From the data in cols. 3 and 4 it can be seen that the difference of the dispersion effects is only 3—6 kg.-cals. It might seem dangerous to draw conclusions from a difference which is so small compared with the quantities involved, but it is evident that the difference increases as the values assumed for ΔE_{C-O} or ΔE_{C-H} are increased. As the real ΔE values may be even greater than 11 or 12 e.v. (cf. p. 434), it can be concluded that the dispersion effect corresponding to the "*exo*-intermediate configuration" is not greater than that corresponding to the "*endo*-intermediate configuration." The difference in the total-attraction energy (sum of dispersion effect and dipole-induction energy) is therefore not less than the difference in the dipole-induction energy.

SUMMARY.

London has deduced an approximation formula for the attraction energy for simple molecules, due to the dispersion effect. An attempt is made to extend the use of this formula to the calculation of energies between large organic molecules. In order to test the method the lattice energy of benzoquinone has been calculated. The agreement with the experimental heat of sublimation is satisfactory. For an understanding of the course of diene syntheses (*e.g.*, addition of benzoquinone to *cyclo*pentadiene) it is important to estimate the attraction energies of the reacting molecules in different mutual orientations. The attraction energy due to the dispersion effect between benzoquinone and *cyclo*pentadiene is calculated for three orientations and is compared with the dipole-induction energies.

The author is indebted to Prof. Ingold, F.R.S., Dr. London, Dr. Eisenschitz, and Dr. Robertson for helpful discussions.

UNIVERSITY COLLEGE, LONDON. [*Received, January 18th*, 1936.]

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105. *Relationships between Reaction Velocities and Ionisation Constants.*

By J. F. J. DIPPY and H. B. WATSON.

IN 1933, Hammett and Pfluger (*J. Amer. Chem. Soc.*, 55, 4079) observed a roughly linear relationship between the logarithms of the velocity coefficients (k) for the reactions of certain methyl esters with trimethylamine and those of the dissociation constants (K) of the corresponding acids. The variations in log K and log k represent the changes of the free energy of ionisation and of the energy of activation respectively, provided, in the latter case, that the value of the non-exponential term in the Arrhenius equation does not vary seriously. The close similarity between Hammett and Pfluger's reaction and the process of ionisation is obvious from the equations (referring to benzoic acids and esters):

$$C_6H_4X{\cdot}CO_2Me + NMe_3 = C_6H_4X{\cdot}COO^- + NMe_4^+$$
$$C_6H_4X{\cdot}CO_2H + H_2O \rightleftharpoons C_6H_4X{\cdot}COO^- + H_3O^+.$$

A reagent removes a positively charged methyl group or a hydrogen ion respectively, and the position of the variable substituent X with respect to the ion removed is identical in the two cases. The approximate proportionality between the increments of energy due to the same substituent is not surprising, therefore, since polar effects of any character, whether they be induced polarisations, direct field effects, or electromeric displacements, have equal opportunity of transmission in each of the three reactions represented above. In a later contribution, Hammett (*Chem. Reviews*, 1935, 17, 125) noted a similar connexion

between the ionisation constants of bases $C_6H_4X{\cdot}NH_2$ and the velocity coefficients of several reactions of the type

$$C_6H_4X{\cdot}NR_2 + R{\cdot}Hal = C_6H_4X{\cdot}NR_3^+ + Hal^-$$

which is clearly comparable with

$$C_6H_4X{\cdot}NH_2 + H{\cdot}OH \rightleftharpoons C_6H_4X{\cdot}NH_3^+ + OH^-.$$

Finally, similar remarks are found to apply (Hammett, *loc. cit.*) to a third type of reaction, represented by the alkaline hydrolysis of *m*- and *p*-substituted benzoic and phenylacetic esters, where the plot of log k against log K for the *corresponding* acid (benzoic or phenylacetic) is approximately linear. In all these examples, the substituent is situated in the same position with respect to the point of reaction as it is in the acid or base with which comparison is made, and hence all effects have equal chances of transmission in the two cases. Hammett further cites instances of reactions where a comparable connexion exists between oxidation potentials and velocities of oxidation or reduction.

Burkhardt, Ford, and Singleton (this vol., p. 20; cf. Burkhardt, *Nature*, 1935, **136**, 684) have recently sought to extend Hammett's relationship between reaction velocities and dissociation constants of acids, and have obtained, for a number of side-chain reactions, a roughly linear plot of log k (and also of log K for a series of substituted phenylacetic acids) against log K for the corresponding benzoic acids. They include, however, certain systems where all the effects originating at the substituent group are not likely to be transmitted to the same extent as in the benzoic acids employed as reference series.

Very shortly before the appearance of Hammett and Pfluger's original observation, Nathan and Watson (J., 1933, 893) pointed out that an accurate connexion exists between the dissociation constants of a series of substituted acetic acids and the dipole moments of the corresponding methanes; the plot of log K against μ gives a smooth curve of the form

$$\log K = \log K_0 - x(\mu + a\mu^2) \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where K and K_0 refer to the substituted and the unsubstituted acids respectively, and x and a are constants. The relationship was extended by Dippy and Watson (*Chem. and Ind.*, 1935, **54**, 735) to *m*- and *p*-substituted benzoic and phenylacetic acids (using the older "classical" constants in the former case), where certain reservations were necessary, as would be anticipated. In a saturated aliphatic compound the dipole moment is a measure of the inductive effect of the substituent, but when the group is attached to the aromatic nucleus, resonance phenomena (mesomeric effects) are also included (Ingold, *Ann. Reports*, 1926, **23**, 149; J., 1933, 1120; *Chem. Reviews*, 1934, **15**, 253; Sutton, *Proc. Roy. Soc.*, 1931, **133**, *A*, 668; Bennett, *Ann. Reports*, 1929, **26**, 132; Bennett and Glasstone, *Proc. Roy. Soc.*, 1934, **145**, *A*, 71). Nevertheless, the dipole moment is the best measure of the permanent polarisation set up by a group, and, since the dissociation constants of the saturated aliphatic acids are related in a simple manner to the dipole moments of substituted methanes, the application of the same expression to aromatic acids and the corresponding benzene derivatives is likely to provide useful evidence regarding electromeric or other variable effects which operate when the group is in aromatic combination. The plot of dissociation constant against dipole moment should, in fact, illustrate very clearly the peculiarities of certain groups, and it is satisfactory to note that, when such a plot was prepared (Dippy and Watson, *loc. cit.*), the anticipated divergences were found. Accurate thermodynamic constants for a further number of substituted benzoic acids (in water at 25°) have recently become available as the result of work in these laboratories, and a better test of the relationship is now possible. The graph (Fig. 1) is very similar to that obtained by use of the older classical constants. The special features of the groups which cause deviations have already been discussed (Dippy, Watson, and Williams, J., 1935, 346).

A quantitative relationship between dipole-moment values and a suitable function of reaction velocities was also observed by Nathan and Watson (J., 1933, 890, 1248; *Nature*, 1934, **133**, 379). Continuing this work, Evans, Morgan, and Watson (J., 1935, 1174) found that, in three cases where energies of activation were known for the same reaction of a

whole series of *m*- and *p*-substituted benzene derivatives, the expression $E = E_0 - C(\mu + b\mu^2)$ is applicable except for substituents which give rise to effects not included in the measured moment (the constant C may have either a positive or a negative sign, according as the reaction is of Type A or B). Further, when it is assumed that log k is a measure of E (the changes in the collision term due to variations of molecular weights and diameters are inappreciable), a number of other reactions, for which data at one temperature only are available, conform to the same formula. Hence, for a given reaction of a series of *m*- or *p*-substituted compounds, where the non-exponential term of the Arrhenius equation does not vary seriously, the connexion between velocity coefficients and the dipole moments of the appropriate substituted benzenes is

$$\log k = \log k_0 - y(\mu + b\mu^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the reservations noted above being necessary for some groups.

FIG. 1.

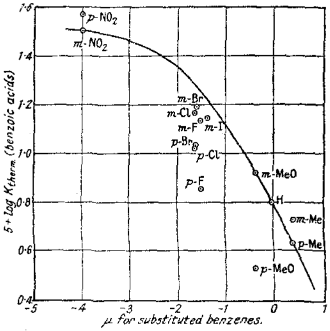
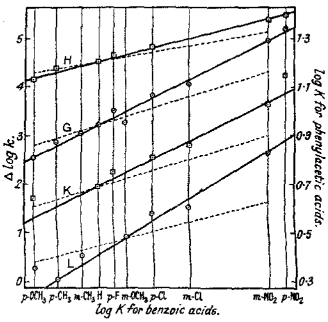


FIG. 2.



Values of K are due to Dippy and Williams (J., 1934, 1888; 1935, 343) and Dippy and Lewis (in the press); μ values are from tables in *Trans. Faraday Soc.*, Sept. 1934; all were obtained by the optical method in benzene at about 20°. The " effective moment " for $-OCH_3$ is taken as $\mu \times \cos 105°$ (compare Nathan and Watson, *Nature*, 1934, **133**, 379; Evans, Morgan, and Watson, J., 1935, 1177).

It is interesting to consider whether the relationship between reaction velocities and dissociation constants, as observed by Hammett, and extended by Burkhardt, Ford, and Singleton, follows as a deduction from equations (1) and (2). These equations being written in the form $\Delta \log K = -x(\mu + a\mu^2)$ and $\Delta \log k = -y(\mu + b\mu^2)$, combination of the two gives

$$\Delta \log k = (y/x)\, \Delta \log K + y(a - b)\mu^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation refers to polar effects of a permanent nature only, and it is evident that, if only these effects are operative, equations (1) and (2) indicate a linear relationship between log k and log K if $a = b$, *i.e.*, if the coefficients of the μ^2 term are the same for the process under consideration as for the acids of the reference series. We have calculated the following values from the data for dissociation constants of benzoic acids in water at 25° (Dippy and Williams, J., 1934, 1888; 1935, 343; Dippy and Lewis, in the press), alkaline hydrolysis of benzoic esters in 88% alcohol at 30° (G; Kindler, *Annalen*, 1926, **450**, 1; 1927, **452**, 90; 1928, **464**, 278), alkaline hydrolysis of cinnamic esters under the same conditions (H; Kindler, *ibid.*), dissociation constants of phenylacetic acids in water at 25° * (K;

* The remarks concerning the velocity coefficients of the other processes are equally applicable here: Δ log k in equation (3) becomes Δ log K', where K' is the dissociation constant of a substituted phenylacetic acid.

Dippy and Williams, J., 1934, 161, 1888; 1935, 343), and the prototropy of the αγ-diphenylmethyleneazomethine system in alcohol at 82° catalysed by sodium ethoxide (L; Shoppee, J., 1931, 1225; 1932, 696):

Benzoic acids	$\log K = \log K_0 - 0{\cdot}402\,(\mu + 0{\cdot}14\mu^2)$
G	$\log k = \log k_0 - 0{\cdot}625\,(\mu + 0{\cdot}069\mu^2)$
H	$\log k = \log k_0 - 0{\cdot}356\,(\mu + 0{\cdot}096\mu^2)$
K	$\log K = \log K_0 - 0{\cdot}125\,(\mu + 0{\cdot}076\mu^2)$
L	$\log k = \log k_0 - 0{\cdot}504\,(\mu + 0{\cdot}0096\mu^2)$

Although the coefficients of the μ^2 term are of the same order of magnitude, there is an appreciable variation.

If, however, the Hammett relationship is to be general, there must also be *either* the absence of *or* a strict proportionality between effects not included in the dipole moment. The operation of electromeric effects is proved by the deviation from the dipole-moment expression (and even sequence) of acids and other compounds having substituents such as *p*-OCH_3; the proportionality or otherwise of these effects in the different systems considered will be indicated by the extent to which Hammett's relationship applies to such cases.

Both Hammett and Burkhardt employed the older classical values for the dissociation constants of substituted benzoic acids; these are, of course, not accurate, and sometimes are not comparable. It might be thought, therefore, that the appreciable and sometimes even serious deviations from the linear relationship, as found by Hammett and by Burkhardt, are due to the uncertainty of the values of the dissociation constants. Any doubt arising from this cause can now be removed, however, by constructing a plot using our accurate thermodynamic constants, all obtained by an identical procedure; relationships observed under such conditions may be regarded with confidence. In Fig. 2 the relevant data for processes G, H, K, and L are plotted against these values. These particular sets of data have been selected for the test because (*a*) there is every reason to believe that they are accurate, (*b*) the differences between the highest and lowest values of the velocities (or equilibrium constants in case K) are suitably large, and (*c*) data for a whole series of substituted derivatives are available. It is clear from the figure that, when the accurate constants are used, a number of the points fall very near to straight lines (the continuous lines in Fig. 2), but also that there are still serious divergences. It might be urged that, in G, H, and L, these *could* be attributed to variations in the non-exponential term of the Arrhenius equation, or differences of temperature or medium, but this is certainly not the case in K, where the points refer to the dissociation constants of substituted phenylacetic acids, obtained by a technique and under conditions identical with those employed for the benzoic acids. The linear relationship is clearly only a rough approximation.

The positions of the points referring to *p*-methoxy-substituted compounds show that in some cases (G and H), as would be expected, the electromeric effects are almost proportional to those operating in the benzoic acid series, while in others (K and L) they are not, as would again be anticipated from the different possibilities of transmission. It may be pointed out that Hammett plotted velocities of hydrolysis of phenylacetic esters against the dissociation constants of the *same* acids and not against benzoic acids.

The broken lines in Fig. 2 are those which would be obtained if the coefficients of μ^2 were the same in all cases; these are quite different from the lines (continuous in Fig. 2) which pass most closely to the points for any given reaction. The arrangement of the points round straight lines is thus not an obvious deduction from the dipole-moment relationship.

The use of accurate dissociation constants for the acids of the reference series enables us, therefore, to state the following conclusions with some degree of certainty:

1. A connexion of a roughly linear character exists, in a number of cases, between the values of log *k* for the same reaction of a series of *m*- or *p*-substituted benzene derivatives and those of log *K* for the corresponding benzoic acids.

2. This connexion does not follow from the known relationships of velocity coefficients

and dissociation constants with dipole moments; it may, perhaps, arise from the approximate balancing of opposing effects.

3. In some reactions electromeric effects cause divergence from the linear relationship, exactly as they do from the dipole-moment expression; clearly, this must occur except in cases where identical paths are available, in the compounds compared, for the transmission of these effects.

4. The relationship of reaction velocities either with dissociation constants or with dipole moments is no doubt conditional upon the absence of serious variations in the non-exponential term of the Arrhenius equation.

THE TECHNICAL COLLEGE, CARDIFF. [*Received, February 19th*, 1936.]

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106. *Further Examples of the Use of Paramagnetism as a Test for Free Radicals.*

By F. L. ALLEN and S. SUGDEN.

IN continuation of our work on the magnetism of organic substances which contain an odd number of electrons (Kenyon and Sugden, J., 1932, 170; Sugden, *Trans. Faraday Soc.*, 1934, **30**, 18) we have examined the susceptibility of the substances referred to below. The molecular susceptibility should be given by $\chi_M = \chi_\mu + \chi_d + \chi_r$, where χ_d is the diamagnetic contribution, which can be computed with sufficient accuracy by adding Pascal's constants for the atoms and links in the molecule, and χ_r is a small residual term due to "high frequency" elements in the quantum-theory treatment (van Vleck, "Theory of Electric and Magnetic Susceptibilities," 1932, p. 274) which can be neglected in a discussion of strongly paramagnetic substances; χ_μ can therefore be obtained as the algebraic difference between χ_M and χ_d, and the effective magnetic moment is then given by $\mu_{eff.} = 2{\cdot}83\sqrt{\chi_\mu T}$. For a free radical with one electron with an unbalanced spin at 20°, χ_μ should be 1270×10^{-6} e.m.u. and $\mu_{eff.}$ should be 1·73 Bohr magnetons.

		$t.$	χ.*	χ_M.	χ_d.	χ_μ.	$\mu_{eff.}$.
1	$Ph_2N{\cdot}\dot{N}{\cdot}C_6H_2(NO_2)_3$	16°	2·30	906	−212	1118	1·61
1a	$Ph_2N{\cdot}NH{\cdot}C_6H_2(NO_2)_3$	16	−0·537	−215	—	—	—
2	$(p\text{-}NO_2{\cdot}C_6H_4)_3C—$	18	1·723	651	−141	792	1·36
2a	$(p\text{-}NO_2{\cdot}C_6H_4)_3CBr$	16	−0·376	−172	—	—	—
3	$Ph_2C—O—K$	17	3·546	784	−124	908	1·45
3a	$Ph_2C{=}O$	17	−0·594	−108	—	—	—

* All susceptibilities are recorded in e.m.u. $\times 10^{-6}$.

The above table contains the data for three substances which we have found to exhibit a large paramagnetism *in the solid state. αα-Diphenyl-β-trinitrophenylhydrazyl* (No. 1) appears to be a very stable free radical (see below) and, from the observed paramagnetism, contains at least 90% of the free radical form in the solid state. The diamagnetic correction for this substance was calculated from the susceptibility of the parent hydrazine (No. 1a) which, as theory predicts, is diamagnetic. Since this work was completed E. Müller, Müller-Rodloff, and Bunge (*Annalen*, 1935, **520**, 235) have published observations on the magnetic susceptibility of a number of substances including the hydrazyl (1) and conclude that it is entirely in the free-radical form.

Substance No. 2 is of interest since it is of the triphenylmethyl type. Its large paramagnetism shows that in the solid state it consists largely of the free radical. The low values found for the susceptibility and the moment are probably due to oxidation during the handling of this very unstable substance in spite of the precautions taken to avoid exposure to air. The diamagnetic correction for this compound was obtained from the susceptibility of the parent bromide (No. 2a) by taking Br as − 30·6.

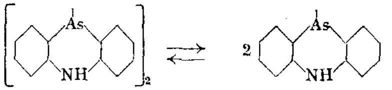
The ketyl (No. 3) has already been shown to be paramagnetic in dioxan solution (Sugden, *loc. cit.*), and is now found to be so in the solid state also. The susceptibility found for the solid is a little lower than that found in solution; it may be interpreted as indicating

at least 70% of free radical. This is a minimum estimate, since any oxidation would give too low a value.

The relative stabilities of the hydrazyl (1) and the triphenylmethyl derivative (2) were studied by measuring specimens stored in corked tubes from time to time. The following results were obtained.

	αα-Diphenyl-β-trinitrophenylhydrazyl.				*Tri*-p-*nitrophenylmethyl.*		
Time (days)	0	2	7	42	0	2	9
χ_M	1118	1123	1117	1082	792	270	16

We have also examined two other substances which might be free radicals, but with negative results. 10 : 10′-Bis-5 : 10-dihydrophenarsazine (I) from its orange-yellow colour and its ready oxidation might be supposed to exist to some extent in the solid state as the free radical (II). We are indebted to Prof. C. S. Gibson, F.R.S., for a specimen of the parent chloride from which the phenarsazine was prepared. The phenarsazine was

(I.)  (II.)

found to be diamagnetic ($\chi = -0{\cdot}764$), hence the solid must consist of the dimeric form (I) with no detectable amount of the free radical (II).

On both chemical and physical grounds it has been suggested that thiobenzophenone is a biradical Ph_2C—S (Bergmann, Magat, and Wagenburg, *Ber.*, 1930, **63**, 2576; Hunter and Partington, J., 1933, 87). We have found, however, that it is diamagnetic with a mass susceptibility of $-0{\cdot}677$. E. Müller and Müller-Rudloff (*Ber.*, 1935, **68**, 1276) also find from the susceptibility of *pp*′-tetramethyldiaminothiobenzophenone that it exists to the extent of less than 1% as free radical in chloroform solution. It should, however, be noted that in these substances two free electrons are present in the biradical, and if their spins are opposed then no paramagnetism would result. The magnetic test is therefore not decisive for biradicals.

Experimental.

Magnetical susceptibilities were measured by the Gouy method as described earlier (J., 1932, 163).

αα-Diphenyl-β-trinitrophenylhydrazyl. The parent hydrazine, m. p. 173° (decomp.), was prepared by condensation of αα-diphenylhydrazine with picryl chloride. Oxidation of this with lead peroxide (Goldschmidt and Renn, *Ber.*, 1922, **55**, 636) afforded the hydrazyl as violet-black prisms, which were crystallised from chloroform–ether; m. p. 138—140°.

Tri-p-*nitrophenylmethyl.* Tri-*p*-nitrophenylmethane, prepared by the method of Hantzsch and Hein (*Ber.*, 1919, **52**, 495), was converted into the dark green free radical in an atmosphere of nitrogen as described by Ziegler and Boye (*Annalen*, 1927, **458**, 252).

Benzophenone-potassium. 12 G. of benzophenone in 120 c.c. of dry ether were shaken with 2·5 g. of potassium dust for 2 hours in an atmosphere of nitrogen. The deep blue precipitate was dried in a current of nitrogen, the measurement tube quickly fitted to the vessel containing the ketyl, and the substance packed evenly into the tube by means of a glass rod passing through a rubber sleeve in the preparation vessel. A current of nitrogen was passed continuously through the apparatus to minimise decomposition.

10 : 10′-Bis-5 : 10-dihydrophenarsazine was prepared from the chloride by reduction with hypophosphorous acid (Burton and Gibson, J., 1926, 2246) and obtained as orange needles, m. p. 306—307°. Its solutions in acetone, alcohol, or benzene did not darken on heating.

Thiobenzophenone was prepared as described in "Organic Syntheses," XI, 94. The deep blue product was recrystallised three times from ligroin and melted at 53°.

Birkbeck College, London, E.C. 4. [*Received, March 2nd*, 1936.]

107. *The Glucosides of* Strophanthus Emini.

By I. D. LAMB and S. SMITH.

SOME years ago the Director of the Imperial Institute suggested that the seeds of *Strophanthus Emini* might be considered by the Pharmacopœia Commission as an alternative to the seeds of *S. kombé*, which are alone official. With this end in view the Commission arranged for investigations of the chemistry, pharmacognosy, pharmacology, and clinical use of the drug, which have been partly reported elsewhere (Anon., *Quart. J. Pharm.*, **1935**, 61; Lamb and Smith, *ibid.*, p. 71).

When the investigation was started, comparatively little was known of the glucosides of this species and the presence of strophanthin in *S. Emini* had been both denied and affirmed. While the work was in progress an important paper by Jacobs and Bigelow (*J. Biol. Chem.*, 1932—3, **99**, 521) appeared. The strophanthin which they isolated consisted of a complex mixture, which was divided into two classes according to the ease of hydrolysis by acids. The more easily hydrolysable glucosides are glucosides of an *a*-deoxy-sugar and on hydrolysis give a mixture of strophanthidin and periplogenin. The less easily hydrolysable glucosides give a monoside, $C_{30}H_{46}O_9$, soluble in chloroform, and a bioside, $C_{36}H_{56}O_{14}$, sparingly soluble in chloroform, both of which are derivatives of the same genin $C_{23}H_{34}O_5$. The last was isolated only as the trianhydrogenin $C_{23}H_{28}O_2$, isomeric but not identical with trianhydroperiplogenin. The sugar in the monoside appeared to be isomeric or identical with digitalose and the bioside contains an additional hexose, possibly glucose.

For the present investigation the seeds of *S. Emini* were supplied by the Director of Agriculture, Tanganyika, through the courtesy of the Director of the Imperial Institute. One lot of seeds, at least five years old, and two subsequent lots, specially collected and worked up soon after receipt, all gave similar results. The "strophanthin" prepared as previously described (Lamb and Smith, *loc. cit.*) consisted of a complex mixture of amorphous water-soluble glucosides which contained 3—5% of the acetyl group. In this respect it resembles the strophanthins of *S. kombé* and *S. sarmentosus*, which we examined for comparison and also found to contain acetylglucosides, the presence of which has not hitherto been recorded in strophanthin. A small portion of the glucosides was soluble in chloroform and consisted of a mixture of monosides, from which was isolated a small amount of cymarin. As the amorphous material did not lend itself to fractionation, it was subjected to enzyme hydrolysis by the method used by Jacobs and Hoffmann (*J. Biol. Chem.*, 1926, **69**, 153) in the investigation of other species of *Strophanthus*. By this means the greater part of the complex glucosides was converted into monosides soluble in chloroform. A part which was incompletely hydrolysed gave a crystalline water-soluble glucoside, which has not yet been obtained pure. It appears to consist of a mixture of a bioside formed from emicymarin (see below) and glucose and its acetate. The monosides consisted of a mixture which on crystallisation gave some initial crops which could not be separated into pure glucosides, but which on hydrolysis gave a mixture of strophanthidin and periplogenin with the sugar cymarose. Subsequent crops gave a new glucoside which, since it seems to be characteristic of *S. Emini*, is named *emicymarin*.

Emicymarin, $C_{30}H_{46}O_9$, is a typical monoside of the heart poison group. Like the other cardio-tonic glucosides, it is a lactone and gives the Legal reaction for Δ^{β}-unsaturated lactones (Jacobs, Gustus, and Hoffmann, *J. Biol. Chem.*, 1926, **67**, 333; **70**, 1). It does not form an oxime. When the double bond is saturated either by reduction or by isomerisation, the respective products no longer give the Legal reaction. It forms a *diacetate*. Emicymarin is unchanged by the gentle conditions of hydrolysis which hydrolyse glucosides, such as cymarin and periplocymarin, which contain α-deoxy-sugars. More drastic conditions of hydrolysis give rise to a trianhydrogenin, $C_{23}H_{28}O_2$, identical with trianhydroperiplogenin, a *monoanhydrogenin*, $C_{23}H_{32}O_4$, and a sugar, digitalose, which has been obtained crystalline for the first time and identified by conversion into digitalonolactone.

Jacobs and Bigelow (*loc. cit.*) have already suggested that the glucosides which they isolated might be glucosides of *allo*periplogenin. The seeds of *S. Emini* have therefore been subjected to the process carried out by Jacobs (*J. Biol. Chem.*, 1930, **88**, 519) with *S. kombé*

seeds. After this allomerisation process a mixture of sparingly soluble monosides was obtained, from which the monoside of Jacobs and Bigelow was isolated in addition to the above-mentioned glucoside. The same monoside was obtained when emicymarin was subjected to the action of the marc from *S. Emini* seeds and it is therefore *allo*emicymarin.

*allo*Emicymarin on hydrolysis gave the trianhydrogenin $C_{23}H_{28}O_2$ described by Jacobs and Bigelow and in addition a monoanhydrogenin, $C_{23}H_{32}O_4$. The sugar is identical with that from emicymarin, *viz.*, digitalose.

EXPERIMENTAL.

The crushed seeds, freed from fat by light petroleum, were extracted with 90% alcohol. The extract was treated with basic lead acetate and after filtration the excess of lead was removed with hydrogen sulphide. The liquor was evaporated nearly to dryness in a vacuum. The residue was dissolved in water and extracted with chloroform, the extract dried (anhydrous sodium sulphate) and concentrated, and the glucosides precipitated by the addition of light petroleum. The chloroform-soluble fraction amounted to 0·09% of the fat-free seeds. The aqueous liquor was saturated with ammonium sulphate. The water-soluble glucosides separated as a sticky mass, which was collected and extracted with dehydrated alcohol. After filtering from ammonium sulphate, the alcoholic liquor was evaporated to dryness under reduced pressure. The residual amorphous water-soluble glucosides amounted to 4·2% of the fat-free seeds and contained approximately 4% of acetyl.

Isolation of Cymarin.—The chloroform-soluble glucosides from 7 kg. of fat-free seeds after two crystallisations from methyl alcohol gave 2·25 g. of cymarin identical with cymarin from *S. kombé*. It melted at 142—150° and gave a bluish-purple Keller reaction. The anhydrous glucoside had $[\alpha]_{5461}^{20^\circ} + 45{\cdot}0^\circ$, $[\alpha]_D^{20^\circ} + 38{\cdot}4^\circ$ ($c = 1{\cdot}5$ in absolute alcohol). Anhydrous cymarin prepared from *S. kombé* seeds had $[\alpha]_{5461}^{15^\circ} + 45{\cdot}5^\circ$, $[\alpha]_D^{17^\circ} + 39{\cdot}2^\circ$ ($c = 1{\cdot}9$ in absolute alcohol) (Found for the dried substance : C, 65·6; H, 8·2; OMe, 6·0. Calc. for $C_{30}H_{44}O_9$: C, 65·6; H, 8·1; OMe, 5·7%). For further comparison the cymarin from each source was converted into strophanthidin. Alone or when mixed, both specimens melted at 161—165°. The strophanthidin from *S. Emini* had $[\alpha]_{5461}^{15^\circ} + 45^\circ$, $[\alpha]_D^{15^\circ} + 38^\circ$ ($c = 1{\cdot}14$ in 95% alcohol), and that from *S. kombé* had $[\alpha]_{5461}^{20^\circ} + 48^\circ$, $[\alpha]_D^{20^\circ} + 41^\circ$ ($c = 1{\cdot}04$ in 95% alcohol). The identity was confirmed by conversion into the methylal of the dianhydro-derivative by the method described by Jacobs and Bigelow (*loc. cit.*). Alone or mixed, both specimeus melted at 253°.

Enzyme Hydrolysis of the Amorphous Water-soluble Glucosides.—The enzyme was prepared from *S. Emini* seeds by the method given by Jacobs and Hoffmann (*J. Biol. Chem.*, 1926, **69**, 157). A mixture of the amorphous glucosides (10 g.) and crude enzyme (5 g.) in water (700 c.c.) at p_H 5·6 was left at 37° for 9 days. The reducing sugar formed was equivalent to 2·38 g. of glucose determined by the Bertrand micro-method (*Mikrochemie*, 1931—2, **10**, 133). The mixture was treated with five volumes of alcohol, filtered through kieselguhr, and evaporated to small bulk under reduced pressure. The residue was extracted with chloroform. The aqueous layer was saturated with ammonium sulphate, which precipitated the water-soluble glucosides (2·4 g.). These were redissolved in water, and the solution partially saturated with ammonium sulphate. On standing, a water-soluble crystalline glucoside separated as a mass of micro-needles. The chloroform-soluble glucosides (4·3 g.) were crystallised from methyl alcohol. The first crops yielded 2·1 g. of a mixture of glucosides, and the mother-liquors 0·55 g. of crude emicymarin. *The easily hydrolysed monosides.* The mixture referred to above had a lower rotation than pure cymarin and judging by the analytical results was a mixture of two similar glucosides. Various attempts to isolate the pure glucosides failed. The material was hydrolysed by the method used by Windans and Hermanns (*Ber.*, 1915, **48**, 979). The aglucone mixture so obtained also could not be separated by crystallisation, but separation was effected by formation of the oxime. The aglucone, hydroxylamine hydrochloride, and fused sodium acetate (0·01 mol. of each) in 50 c.c. of alcohol were boiled for 6 hours. When the liquor was concentrated, crude periplogenin separated; it was crystallised from ethyl acetate, dilute alcohol, and methyl alcohol until its properties were constant. They then agreed with those described by Jacobs and Hoffmann for the periplogenin from *Periploca graeca* (*J. Biol. Chem.*, 1928, **79**, 527). The anhydrous aglucone had $[\alpha]_{5461}^{23^\circ} + 37{\cdot}9^\circ$, $[\alpha]_D^{23^\circ} + 31{\cdot}4^\circ$ ($c = 1{\cdot}32$ in alcohol). Jacobs and Hoffmann give $[\alpha]_D^{27^\circ} + 31{\cdot}5^\circ$ ($c = 1{\cdot}04$ in alcohol) (Found for the substance dried at 110° in a vacuum : C, 70·9 ; H, 8·7; OMe, nil; N, *nil*; *M*, by lactone titration, 358. Calc. for periplogenin, $C_{23}H_{34}O_5$: C, 70·7; H, 8·8%; *M*, 390). The benzoate separated from dilute alcohol in

glistening wedge-shaped prisms, m. p. 227° to 233° depending on the rate of heating. Jacobs and Hoffmann describe it as glistening wedges " which when heated rapidly melt at 235."

The strophanthidin oxime contained some impurity, which was removed by repeated crystallisation from alcohol. It crystallised in anhydrous rhombic prisms identical in appearance with strophanthidin oxime from *S. kombé*. It melted at 260—270°. $[\alpha]_{5461}^{24°} + 82·5°$, $[\alpha]_{D}^{24°} + 69·8°$ (c = 1·00 in pyridine). Jacobs and Heidelberger give $[\alpha]_{D}^{23°} + 71·3°$ in pyridine (*J. Biol. Chem.*, 1922, **54**, 253) (Found : C, 65·5; H, 7·9; N, 3·4. Calc. for strophanthidin oxime, $C_{23}H_{33}O_6N$: C, 65·8; H, 7·9; N, 3·3%).

Cymarose was isolated after removal of the aglucones by the method of Windaus and Hermanns (*loc. cit.*). It separated from dry ether in needles, m. p. 82—84°. The melting point varies somewhat with the rate of heating. It was not lowered when the sugar was mixed with cymarose obtained from *S. kombé* cymarin. The substance showed a slight mutarotation. The end rotation was $[\alpha]_{5461}^{24°} + 61·4°$, $[\alpha]_{D}^{24°} + 52·4°$ (c = 2·04 in water). For a specimen of cymarose from *S. kombé* cymarin, $[\alpha]_{5461}^{24°} + 60°$, $[\alpha]_{D}^{24°} + 54°$ (c = 2 in water). Jacobs and Hoffmann (*J. Biol. Chem.*, 1926, **67**, 617) give m. p. 91° and $[\alpha]_{D}^{21°} + 53·4°$. The sugar gave the blue colour in the Keller reaction typical of α-deoxy-sugars (Found : C, 51·6; H, 8·6; OMe, 18·9. Calc. for cymarose, $C_7H_{14}O_4$: C, 51·8; H, 8·7; OMe, 19·1%). The cymarose was not isolated in a sufficiently good yield to prove that it was the only sugar present, but the fact that it crystallised suggests that no other sugar was there.

Emicymarin, $C_{30}H_{46}O_9$, after repeated crystallisation from methyl alcohol separated in rosettes of small stout needles or separate prisms. After being dried, it sintered at 160° and melted indefinitely about 207°. The anhydrous substance has $[\alpha]_{5461}^{20°} + 15·8°$, $[\alpha]_{D}^{20°} + 12·8°$ (c = 2·5 in absolute alcohol). It is readily soluble in ethyl alcohol, methyl alcohol, acetone, and chloroform, but sparingly so in water. Crystallised from methyl alcohol, it contains varying amounts of water and methyl alcohol of crystallisation, the latter being lost slowly on exposure to air. It crystallises from cold dilute alcohol with four molecules of water (Fonnd : H_2O, 11·6. $C_{30}H_{46}O_9,4H_2O$ requires H_2O, 11·6%). It crystallises from ethyl acetate free from solvent. It gives a positive Legal reaction, and with the Keller reaction a ring which with reflected light is brown below and green above. The glucoside dissolves in concentrated sulphuric acid to give an orange solution. It has a bitter taste (Found for the glucoside dried at 120° in a vacuum : C, 65·4; H, 8·6; OMe, 5·8; M, by lactone titration, 517. $C_{30}H_{46}O_9$ requires C, 65·4; H, 8·4; OMe, 5·6%; M, 550).

The glucoside could not be hydrolysed by 30% alcohol containing 7% of hydrochloric acid. It was hydrolysed by boiling 2% hydrochloric acid to digitalose and a resinous aglucone which could not be crystallised. The latter or the glucoside itself, when treated with hot 5% hydrochloric acid, gave a mixture of crude anhydrogenins.

Trianhydroemicymarigenin, $C_{23}H_{28}O_2$.—Emicymarin methyl alcoholate (6·8 g.) in warm alcohol (60 c.c.) was added to 1200 c.c. of boiling 5% hydrochloric acid. A somewhat sticky yellow solid separated immediately. After boiling for 2 minutes, the solution was cooled and kept for some time. The separated solid was recrystallised from alcohol. The crystals (1·96 g.) consisted of a mixture of the trianhydrogenin and another compound similar in properties but having a lower rotation and containing a smaller percentage of carbon. The latter compound has not been obtained pure, but may be the dianhydro-derivative. On recrystallisation the trianhydrogenin collects in the first crops. It may be purified by numerous recrystallisations, but is more readily purified by treatment with acetic anhydride. The crude crystals were warmed on the water-bath for 75 minutes with acetic anhydride (20 c.c.). On cooling, the nearly pure compound separated. It was recrystallised a few times from alcohol and from dilute pyridine until the specific rotation was constant. Trianhydroemicymarigenin crystallises in long, pale yellow needles which sinter at 190° and melt at 192°. The melting point varies somewhat with the rate of heating. It has $[\alpha]_{5461}^{19°} - 167·0°$, $[\alpha]_{D}^{19°} - 138·5°$ (c = 2·45 in pyridine). The substance is sparingly soluble in the usual solvents, but more so in hot alcohol or ethyl acetate. It is readily soluble in pyridine. It dissolves in sulphuric acid to give a reddish-violet colour turning to red. In the Keller reaction a red ring is obtained, the top layer gradually assumes a pale green colour, and the bottom layer a red colour (Found : C, 82·1; H, 8·4; M, by lactone titration, 360. Calc. for $C_{23}H_{28}O_2$: C, 82·1; H, 8·4%; M, 336).

Trianhydroperiplogenin was prepared from the periplogenin from the easily hydrolysed glucosides by the method described by Jacobs and Bigelow (*J. Biol. Chem.*, 1933, **101**, 697), who after one recrystallisation obtained a product which melted at 191—193°, depending on the rate of heating, had $[\alpha]_{5461}^{24°} - 130°$ (in pyridine), and gave the correct analytical figures. After one recrystallisation our material sintered at 184° and melted indefinitely at 194° and had

$[\alpha]_{D}^{22^\circ}$ − 118° (in pyridine). It was purified by treatment with acetic anhydride with subsequent crystallisation from alcohol as carried out in the case of trianhydroemicymarigenin. It separated from alcohol in thin, pale yellow, anhydrous needles which sintered at 187° and melted at 192°. $[\alpha]_{5461}^{22^\circ}$ − 167·0°, $[\alpha]_{D}^{22^\circ}$ − 136·8° (c = 1·76 in pyridine). The colour reaction with sulphuric acid was as described by Jacobs and Bigelow (Found: C, 81·9; H, 8·2. Calc. for $C_{23}H_{28}O_2$: C, 82·1; H, 8·4%). Trianhydroperiplogenin appears to be identical with trianhydroemicymarigenin. The specific rotations, melting points, and the sulphuric acid colour reaction were all similar and a mixture of the two showed no depression of the melting point. Both specimens had the same optical characters under polarised light. The crystals were optically biaxial and showed parallel extinction.

Anhydroemicymarigenin, $C_{23}H_{32}O_4$.—The alcoholic mother-liquors obtained above after removal of the crude crystalline trianhydro-compound were treated with water and the precipitate was dissolved in ethyl acetate. On standing, a small amount of crystals separated. They were recrystallised twice from methyl ethyl ketone. *Anhydroemicymarigenin* forms short white rods, m. p. 269—277°. It has $[\alpha]_{5461}^{24^\circ}$ + 67°, $[\alpha]_{D}^{24^\circ}$ + 59° (c = 3·0 in pyridine). It is sparingly soluble in the usual solvents except pyridine (Found: C, 74·1; H, 8·7. $C_{23}H_{32}O_4$ requires C, 74·1; H, 8·7%).

Digitalose, $C_7H_{14}O_5$.—Emicymarin (3·0 g.) was dissolved in warm alcohol (6 c.c.), water (184 c.c.) and 10% hydrochloric acid (10 c.c.) were added, and the solution was boiled under reflux for 2½ hours. The reducing value of the solution was then constant. The aglucone separated as an oil and was removed by extraction with chloroform. Yield, 1·8 g. The aqueous liquor was treated with silver carbonate to remove hydrochloric acid and then with hydrogen sulphide to remove the excess of silver. After evaporation and drying in a vacuum over sulphuric acid a syrup (0·75 g.) remained. It crystallised from a solution in dry ether on addition of light petroleum. From ethyl acetate it separated in rosettes of needles. The melting point rose when the solid was kept. Originally it sintered at 101° and melted at 106°. After 3 days it melted at 115° and after 4 months at 119°. The specific rotation rose from $[\alpha]_{5461}^{27^\circ}$ + 109° (15 mins. after solution) to $[\alpha]_{5461}^{22^\circ}$ + 126°, $[\alpha]_D$ + 106° (c = 1·7 in water) in 17 hours and was then constant. The reducing value of the sugar was determined by the Bertrand micro-method. Under these conditions 1 mg. had the same reducing value as 0·32 mg. of anhydrous glucose. The Keller reaction was negative. For analysis the sugar was dried at 70° in a vacuum (Found: C, 47·4; H, 7·9; OMe, 17·4. Calc. for $C_7H_{14}O_5$: C, 47·2; H, 7·9; OMe, 17·4%).

Digitalonolactone, $C_7H_{12}O_5$.—The sugar (368 mg.) in water (2·2 c.c.) was shaken with bromine (0·16 c.c.) for 1 hour. After standing over-night, the excess of bromine was removed in a vacuum by a current of air, the hydrobromic acid was removed with silver carbonate, and the excess of silver by hydrogen sulphide. The solution was evaporated on the steam-bath. The residue solidified in small rectangular crystals. After recrystallisation from alcohol it formed long white rhombic needles, m. p. 137—138°. $[\alpha]_{5461}^{19^\circ}$ − 102°, $[\alpha]_{D}^{19^\circ}$ − 83° (c = 3·23 in water). There was a slight fall in rotation when the solution was kept. For analysis the lactone was dried in a vacuum over phosphoric oxide. The lactone group was determined by boiling with excess of N/100-barium hydroxide for 15 minutes (Found: C, 48·0; H, 7·0; OMe, 17·2; M, by lactone titration, 179. Calc. for $C_7H_{12}O_5$: C, 47·7; H, 6·9; OMe, 17·6%; M, 176). For comparison, digitalonolactone was prepared from the mixed sugars from *digitalinum verum* by the method given by Kiliani (*Ber.*, 1930, **63**, 2868). It melted at 135—137° and, mixed with the above lactone, at 135—138°. It crystallised in rhombic needles. $[\alpha]_{5461}^{20^\circ}$ − 102°, $[\alpha]_{D}^{20^\circ}$ − 85° (c = 3·26 in water). Digitalonolactone was described by Kiliani (*Ber.*, 1892, **25**, 2117) as rhombic crystals having $[\alpha]_{D}^{26^\circ}$ − 79·4° (c = 3·36). The melting point was not recorded.

Diacetylemicymarin.—The anhydrous glucoside (0·532 g.) was dissolved in a mixture of pyridine (5 c.c.) and acetic anhydride (2 c.c.). After several hours the mixture was diluted with water. The *acetate* separated in micro-plates. It crystallised from methyl alcohol in anhydrous plates, m. p. (indefinite) *ca.* 278°. $[\alpha]_{5461}^{20^\circ}$ + 27·8°, $[\alpha]_{D}^{20^\circ}$ + 22·8° (c = 1·4 in methyl alcohol) (Found: C, 64·0; H, 7·9; OMe, 5·0; CH_3·CO, 13·9; M, by lactone titration, 210. $C_{34}H_{50}O_{11}$ requires C, 64·3; H, 7·9; OMe, 4·9; CH_3·CO, 13·6%; M, 634).

Dihydroemicymarin.—The anhydrous glucoside (0·46 g.) in 95% alcohol (10 c.c.) was shaken with hydrogen and platinum oxide catalyst (0·5 g.). In 8½ hours 18·7 c.c. of hydrogen at *N.T.P.* were absorbed (Calc. for one double bond, 18·7 c.c.). The alcoholic solution was concentrated and treated with water. The *dihydro-compound* separated in fine needles. The Legal reaction was negative (Found: H_2O, varying from 11·6 to 18·0% depending on the temperature of crystallisation. $C_{30}H_{48}O_9$,$4H_2O$ requires H_2O, 11·5%. $C_{30}H_{48}O_9$,$7H_2O$ requires H_2O, 18·6%).

The anhydrous substance sinters at 147° and melts indefinitely at 151°. It has $[\alpha]_{5461}^{19°} + 11\cdot2°$; $[\alpha]_D^{19°} + 8\cdot6°$ ($c = 6\cdot4$ in alcohol) (Found for material dried at 100° in a vacuum: C, 64·9; H, 8·8; OMe, 5·4. $C_{30}H_{48}O_9$ requires C, 65·2; H, 8·8; OMe, 5·6%).

iso*Emicymarin*.—Anhydrous emicymarin (2·2 g.) was dissolved by warming in methyl alcohol (25 c.c.); methyl alcohol (15 c.c.) containing 2·1 g. of caustic potash was added to the cooled solution. After standing at room temperature for 2 hours, the solution was poured into cold water and acidified (Congo-red) with hydrochloric acid. The iso*glucoside* separated slowly as a mass of fine needles. It contains two molecules of water, which it loses slowly on exposure to air. It is sparingly soluble in water or ethyl alcohol, but more so in methyl alcohol, from which it crystallises in the anhydrous form. It then sinters at 252° and melts at about 270° depending on the rate of heating. The anhydrous *iso*glucoside has $[\alpha]_{5461}^{25°} + 30\cdot9°$, $[\alpha]_D^{20°} + 26\cdot2°$ ($c = 1\cdot7$ in pyridine). The Legal reaction is negative (Found for the substance dried at 100° in a vacuum: C, 65·5; H, 8·3; OMe, 5·6; *M*, by lactone titration, 525. $C_{30}H_{46}O_9$ requires C, 65·4; H, 8·4; OMe, 5·0%; *M*, 550). *iso*Emicymarin was not reduced under the conditions which reduce the normal glucoside. Hydrolysis by boiling 50% alcohol containing 5% of hydrochloric acid gave a small yield of an aglucone, $C_{23}H_{34}O_5$, resembling *iso*periplogenin (Jacobs and Hoffmann, *J. Biol. Chem.*, 1928, **79**, 529). The quantity obtained was too small to make the identification certain. Digitalose also was isolated.

The crystalline water-soluble glucoside separated from hot water in sheaths of white micro-needles, m. p. 205—207°. The material dried at 115° in a vacuum had $[\alpha]_{5461}^{21°} - 2\cdot0°$, $[\alpha]_D^{21°} - 1\cdot7°$ ($c = 5\cdot0$ in 95% alcohol) (Found: C, 60·5; H, 8·2; OMe, 4·7; $CH_3\cdot CO$, 1·6. Calc. for $C_{36}H_{55}O_{14}\cdot CO\cdot CH_3$: C, 60·3; H, 7·7; OMe, 4·1; $CH_3\cdot CO$, 5·7%). The low acetyl figure indicates that the substance is a mixture. Hydrolysis by 0·5% hydrochloric acid at 95° gave a syrup which appeared to be a biose. This was further hydrolysed by 5% sulphuric acid at 100°. From the mixture of sugars obtained, glucosazone was isolated; its identity was confirmed by the mixed melting point (Found: N, 15·8. Calc. for glucosazone: N, 15·6%). Digitalose also was isolated.

Allomerisation Process.—The fat-free seeds (1 kg.) were mixed with water (4 l.) and a little toluene and left at about 25° for 14 days. The mixture was treated with alcohol (15 l.) and filtered. The solution was purified with basic lead acetate, freed from lead, and concentrated. During the evaporation the sparingly soluble *allo*glucosides separated as a pasty solid, which was collected, extracted with chloroform, and crystallised once from dilute alcohol. It then weighed 3·6 g. The original mother-liquor after removal of the *allo*glucosides was extracted with chloroform. This extract was combined with the chloroform extract of the solid and evaporated. The residue (31·5 g.) was dissolved in methyl alcohol; 8·4 g. of crude cymarin then separated. When the methyl-alcoholic mother-liquor was treated with water, 8·7 g. of crude *allo*glucosides were precipitated. The filtrate contained emicymarin.

The final liquor after removal of the chloroform-soluble glucosides yielded 6·8 g. of water-soluble amorphous glucosides. These were dissolved in water, and the solution partially saturated with ammonium sulphate. A small amount of the bioside of Jacobs and Bigelow separated.

The crude *allo*glucosides were fractionally crystallised first from dilute alcohol and then from ethyl acetate and acetone. The less soluble material contained a mixture of at least two glucosides, which have not been separated. It resembled *allo*cymarin and possibly was a mixture of *allo*cymarin and *allo*periplocymarin. From the mother-liquors was obtained a monoside identical with that of Jacobs and Bigelow. It was purified by crystallisation first from dilute alcohol, then from ethyl acetate, and finally from methyl alcohol. It crystallises from dilute alcohol as a mass of micro-needles, from methyl alcohol in small plates or leaflets, and from ethyl acetate in rectangular plates. It is readily soluble in methyl and ethyl alcohols and sparingly soluble in acetone and ethyl acetate. The anhydrous glucoside sinters at 240° and melts at 248°. After crystallisation from dilute alcohol it contains 9% of water and then sinters at 170° and melts at 263°. The anhydrous material has $[\alpha]_{5461}^{23°} + 29\cdot7°$, $[\alpha]_D^{23°} + 24\cdot6°$ ($c = 1\cdot85$ in 95% alcohol). Jacobs and Bigelow's monoside melted at 174—180° and had $[\alpha]_D^{25°} + 22°$ ($c = 0\cdot995$ in 95% alcohol). It gives a positive Legal reaction. The Keller reaction is practically negative. Dissolved in sulphuric acid, it gives a reddish-brown solution. The taste is slightly bitter (Found for the substance dried at 110° in a vacuum: C, 65·0; H, 8·4; OMe, 6·1. Calc. for $C_{30}H_{46}O_9$: C, 65·4; H, 8·4; OMe, 5·6%).

Hydrolysis of allo*Emicymarin*.—The anhydrous glucoside (2·73 g.) in 30% alcohol (158 c.c.) containing 0·5% of hydrochloric acid was heated in the steam-bath for 3½ hours. The aglucone separated as a resin (1·95 g.) which could not be crystallised. It was converted into the anhydro-derivatives by boiling under reflux for 2 hours with methyl alcohol (25 c.c.) containing 6% of

hydrogen chloride. The solution was treated with excess of water, and the precipitate fractionally crystallised first from alcohol and then from ethyl acetate. The trianhydrogenin separated first. The anhydrogenin was obtained from the mother-liquors. The dilute alcoholic liquor obtained during the original hydrolysis was extracted with chloroform to remove traces of the aglucone and the sugar was isolated by the method used in the case of emicymarin. It was identified as digitalose and had the properties described above.

Trianhydro*allo*emicymarin separated from alcohol in faintly yellow leaflets or irregular shaped plates, m. p. 153—156°. $[\alpha]_{5461}^{23°} - 106{\cdot}4°$, $[\alpha]_{D}^{23°} - 83{\cdot}5°$ ($c = 3{\cdot}07$ in pyridine) (Found: C, 81·9; H, 8·5. Calc. for $C_{23}H_{28}O_2$: C, 82·1; H, 8·4%). Jacobs and Bigelow give $[\alpha]_{D}^{27°} - 84{\cdot}6°$ ($c = 1{\cdot}015$ in pyridine) and m. p. 154—156°.

*Anhydro*allo*emicymarin* crystallised from ethyl acetate in nearly colourless needles or rectangular plates, m. p. 208—209°. $[\alpha]_{5461}^{22°} + 157°$, $[\alpha]_{D}^{22°} + 133°$ ($c = 4{\cdot}77$ in pyridine). It dissolved in sulphuric acid to give a yellow-orange solution. In the Keller reaction the top layer was dull green and the bottom layer brown. The substance was anhydrous (Found: C, 74·2; H, 8·7. $C_{23}H_{32}O_4$ requires C, 74·1; H, 8·7%).

Conversion of Emicymarin into allo*Emicymarin.*—The enzyme-containing marc was obtained by extracting powdered defatted *S. Emini* seeds twice with ice-cold water and then further by percolation with 95% alcohol until nearly free from glucosides. Emicymarin methyl alcoholate (0·5 g.) was dissolved in water (150 c.c.) by warming. The strophanthus marc (40 g.) was added together with a few c.c. of toluene, and the mixture left at room temperature for 55 days. Since the marc still contained a trace of glucoside, a duplicate experiment was done without the emicymarin. Both lots were worked up by the method given above under allomerisation. The yields of the crude fractions were:

		Blank.
*allo*Glucosides	0·38 g.	<0·01 g.
Chloroform-soluble glucosides	0·14 g.	0·16 g.
Water-soluble glucosides	0·04 g.	0·05 g.

The *allo*glucosides were crystallised from hot ethyl acetate and gave colourless plates (0·31 g.), m. p. 250—258°. The anhydrous material had $[\alpha]_{5461}^{22°} + 28{\cdot}9°$, $[\alpha]_{D}^{22°} + 24{\cdot}0°$ ($c = 2{\cdot}0$ in 95% alcohol) (Found after drying at 120° in a vacuum: C, 64·9; H, 8·4; OMe, 5·7. Calc. for $C_{30}H_{46}O_9$: C, 65·4; H, 8·4; OMe, 5·6%). When hydrolysed at 100° by methyl alcohol containing 6% of hydrogen chloride, the glucoside yielded a small amount of an anhydrogenin, m. p. 207°. This was identical in appearance and reactions with the anhydrogenin from *allo*emicymarin and a mixture of the two melted at 208° (Found: C, 74·6; H, 9·0. Calc. for $C_{23}H_{32}O_4$: C, 74·1; H, 8·7%).

Glucose from E. Strophanthin.—The isolation was difficult, since on acid hydrolysis a mixture of sugars was obtained. It was expected that enzyme hydrolysis of the total glucosides would, after removal of the glucosides, give a solution containing glucose, but the presence of impurities prevented its isolation. The solution, however, yielded an osazone which was identified as glucosazone by its appearance, m. p. and mixed m. p. The rotation of the osazone was determined. 0·15 G. in 5 c.c. of pyridine and 10 c.c. of alcohol in a 2 dcm. tube had an initial rotation $\alpha_{5461}^{23°} - 1{\cdot}73°$. After 24 hours the value had dropped to $- 0{\cdot}98°$. Under the same conditions pure glucosazone gave the values $- 1{\cdot}71°$ and $- 0{\cdot}91°$ respectively.

We wish to express our thanks to Dr. C. H. Hampshire, Secretary to the Pharmacopœia Commission, at whose invitation we began this investigation, and to the Director of Agriculture, Tanganyika, and the Director of the Imperial Institute for a generous supply of *S. Emini* seeds. We wish also to acknowledge the assistance of Mr. T. Dewing, M.Sc., and our indebtedness to Mr. A. Bennett and Mr. H. C. Clarke, who carried out the micro-analyses.

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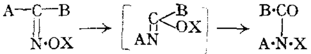
108. *Studies of the Beckmann Change. Part IV. Some Effects of Substitution on the Rate of Rearrangement of Ketoxime Picryl Ethers. A Suggested Mechanism of the Transformation.*

By Arthur W. Chapman and Frederick A. Fidler.

In previous papers of this series (J., 1933, 806; 1934, 1550; 1935, 1223) it has been shown that certain esters and ethers derived from ketoximes undergo a spontaneous Beckmann transformation at room temperature or when heated, and that this rearrangement consists of an intramolecular exchange of positions by one of the hydrocarbon radicals (A) attached to the central carbon atom of the ester molecule (I) and the acyloxy or related group OX.



(I.) (II.) (III.)

Ketoximes themselves are only transformed in the presence of a reagent, the function of which appears to be the formation with the oxime of an ester-like substance capable of undergoing the spontaneous change. This applies, not only to reagents such as phosphorus pentachloride or benzenesulphonyl chloride, but also to the more complex course of the rearrangement under the influence of hydrogen chloride.

Whilst, however, the general character of the rearrangement and the function of the reagent had become clear, more precise knowledge was lacking as to the means by which the groups A and OX exchange places within the molecule, and it seemed possible that some light might be thrown upon this internal mechanism by an investigation of the effects of substitution upon the rate of transformation and upon the energy of activation of the rearrangement.

Three complete series of oxime picryl ethers (V)—(VII) (Y = Cl, NO_2, and Me) and one further disubstituted compound (VII; Y = OMe) were therefore prepared and studied. In addition, two other ethers derived from benzophenoneoxime (IV; with 2 : 4 : 6-trinitro-*m*-tolyl and 2 : 4-dinitrophenyl in place of picryl) were examined.

$C_6H_5{\cdot}C{\cdot}C_6H_5$	$(p)Y{\cdot}C_6H_4{\cdot}C{\cdot}C_6H_5$	$C_6H_5{\cdot}C{\cdot}C_6H_4Y(p)$	$(p)Y{\cdot}C_6H_4{\cdot}C{\cdot}C_6H_4Y(p)$
N·OPic	N·OPic	N·OPic	N·OPic
(IV.)	(V.)	(VI.)	(VII.)

The velocities of rearrangement of the chloro- and methyl-substituted compounds into the corresponding anilides (III) were measured in carbon tetrachloride solutions of two or three different concentrations at several temperatures. The values at each temperature were extrapolated to give the velocity at infinite dilution (k_0), and from these values the energy of activation of the rearrangement as brought about by collision with molecules of carbon tetrachloride was calculated (cf. Part II, *loc. cit.*, p. 1551). Measurements of the rates of rearrangement of benzophenoneoxime picryl ether have already been published (Parts I and II), but a number of these were repeated and substantially confirmed, with a small correction for the value of E.

The results of the measurements on two complete series of oxime picryl ethers are in the following tables (t = temperature; k_0 calculated with time in seconds and Napierian logarithms, and E derived from the slope of the line obtained by plotting log k_0/η against $1/T$).

From these observations certain conclusions immediately emerge. The introduction of the electron-attracting chlorine atom into either phenyl group of the ketoxime retards the transformation, whereas the electron-repelling methyl group accelerates it. Moreover, the introduction of a substituent into the migrating nucleus has a much greater effect on the rate of transformation than a similar substitution in the stationary nucleus. The influence of the polar character of the substituent on the ease of rearrangement was demonstrated even more strikingly by the behaviour of the remaining compounds. The picryl ether of *p*-nitrobenzophenone-α-oxime (VI; Y = NO_2) was isomerised much less readily

Picryl ether of :	Benzophenone-oxime.		*p*-Chlorobenzophenone *a*-Oxime.		*p*-Chlorobenzophenone *β*-Oxime.		Di-*p*-chloro-benzophenone-oxime.	
Hydrocarbon group, migrating	C_6H_5		C_6H_5		*p*-C_6H_4Cl		*p*-C_6H_4Cl	
Hydrocarbon group, stationary	C_6H_5		*p*-C_6H_4Cl		C_6H_5		*p*-C_6H_4Cl	
	t.	$k_0 \times 10^5$.	*t*.	$k_0 \times 10^5$.	*t*.	$k_0 \times 10^5$.	*t*.	$k_0 \times 10^5$.
	70·4°	1·55						
	80·5	4·65	85·8°	3·6	90·8°	2·8		
	90·7	13·2	95·0	9·45			90·8°	1·32
	100·45	36·4	99·8	15·4	100·8	7·74	100·0	3·24
	(cf. also Part II)		105·3	29·7	104·5	11·4		
					110·6	20·6	110·3	11·4
					115·3	31·5	115·5	17·7
E (cals./g.-mol.)	29,200		30,800		30,200		31,500	

Picryl ether of :	Phenyl *p*-tolyl ketone *a*-Oxime.		Phenyl *p*-tolyl ketone *β*-Oxime.		Di-*p*-tolyl ketoxime.	
Hydrocarbon group, migrating	C_6H_5		*p*-C_6H_4Me		*p*-C_6H_4Me	
Hydrocarbon group, stationary	*p*-C_6H_4Me		C_6H_5		*p*-C_6H_4Me	
	t.	$k_0 \times 10^5$.	*t*.	$k_0 \times 10^5$.	*t*.	$k_0 \times 10^5$.
					44·7°	3·0
					50·3	6·25
			55·5°	2·20	60·4	17·1
	65·2°	2·50	65·0	7·94	70·3	55·1
	75·6	7·47	75·3	19·5		
	85·6	18·0	80·4	37·2		
	90·0	32·4				
E (cals./g.-mol.)	26,500		28,300		25,800	

than any of the chloro-compounds, but was converted into p-*nitrobenz*-N-*picrylanilide* (phenyl migrating) by 6 hours' heating at 100° in ethylene dichloride solution. The picryl ethers of the β-oxime and of the dinitro-compound (V and VII) were, however, both recovered unchanged after 6—7 hours' heating at 100° in the same solvent. On the other hand, when attempts were made to prepare di-*p*-anisyl ketoxime picryl ether (VII; Y = OMe) from the oxime, the only product that could be isolated was *p*-anisoyl-*p*-anisidide; rearrangement had evidently occurred at room temperature.

The energies of activation obtained from the measurements of the rates of change vary considerably from the fastest to the slowest transformation. There are minor anomalies in the values of *E* for the α- and the β-oximes of both monosubstituted ketones, but the general trend is clearly for an increase in velocity of rearrangement to be accompanied by a decrease in *E*. The variations in *E* are of the order to be expected if the differences in velocity of rearrangement arise essentially from differences in critical increment.

Over the range of temperatures investigated, the effects of chloro-substitution on the velocity of change were, as shown in the following table, strictly additive (cf. somewhat similar additive effects in a different reaction, Bradfield and B. Jones, J., 1928, 1006; B. Jones, J., 1935, 1831, 1835). In the methyl series the additivity was not so apparent, but the values for these substances are (for reasons discussed in the experimental section) probably less accurate than those for the chloro-compounds. (The values of k_0 used below were read off from the graphs of log k_0 and $1/T$.)

Chloro-compounds.

$10^4/T$	26	27	28
$A = \dfrac{k_0\ \text{(unsubs.)}}{k_0\ (\alpha\text{-chloro-})}$	1·90	2·04	2·45
$B = \dfrac{k_0\ \text{(unsubs.)}}{k_0\ (\beta\text{-chloro-})}$	4·57	4·68	5·00
$A \times B$	8·71	9·55	11·7
$C = \dfrac{k_0\ \text{(unsubs.)}}{k_0\ \text{(dichloro-)}}$	8·51	9·55	11·5

Methyl compounds.

$10^4/T$	28	29	30
$A = \dfrac{k_0\ \text{(unsubs.)}}{k_0\ (\alpha\text{-methyl-})}$	0·41	0·36	0·32
$B = \dfrac{k_0\ \text{(unsubs.)}}{k_0\ (\beta\text{-methyl-})}$	0·13	0·12	0·12
$A \times B$	0·051	0·045	0·038
$C = \dfrac{k_0\ \text{(unsubs.)}}{k_0\ \text{(dimethyl-)}}$	0·036	0·031	0·026

The effects of substitution in the picryl group were less easy to determine, since suitable materials were less readily accessible. The rate of rearrangement of benzophenone-

oxime 2 : 4 : 6-trinitro-*m*-tolyl ether was measured in the same way as for the otber compounds with the following results :

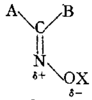
	*2 : 4 : 6-Trinitro-*m*-tolyl ether.*		*Picryl ether.*	
	t.	$k_0 \times 10^5$.	*t.*	$k_0 \times 10^5$.
			80·5°	4·65
	89·4°	2·40*	90·7	13·2
	92·1	3·79		
	95·0	5·10		
	102·8	12·0	100·45	36·4
	104·8	17·0*		
	108·7	22·2 †		
	111·2	34·3 †		
E (cals./g.-mol.)	32,100		29,200	

* 1% Solution. † 0·5% Solution.

The introduction of the electron-repelling methyl group into the picryl radical retarded the transformation, and the retardation was accompanied by an increase in *E* approximately equivalent to the change in rate of rearrangement. This retarding effect of a diminution in the electron-attraction of the picryl group was confirmed by an examination of the 2 : 4-dinitrophenyl ether of benzophenoneoxime which did not rearrange even in nitromethane at 100°.

From these and previous observations it is possible to construct a somewhat more detailed picture of the transformation. The oximes by themselves do not undergo the Beckmann rearrangement, and the activity of the reagents employed to bring about the change can be traced to the formation of compounds of Type (I) where X is an acyl or related group. Such compounds undergo spontaneous isomeric change to (II) and (III) at appropriate temperatures, but only if the group —OX is one having a strong attraction for electrons, as in the esters derived from strong acids. Esters derived from weak acids, like the oximes themselves, can be heated to the temperature of decomposition without rearrangement.

In an oxime ester derived from a strong acid, the attraction for electrons exerted by —OX creates a dipole at —N—O with its positive end at the nitrogen atom (VIII). In consequence of the structure of the oxime ester molecule, the field of the dipole is so oriented that an attraction is set up between the nitrogen atom and those electrons (of the bond A—C) which unite the central carbon atom to the group (A) situated on that side of the molecule away from —OX. If the molecule acquires sufficient energy, this attraction results in the nitrogen atom becoming attached to group A, and the balance of charges is corrected by the migration of —OX to the central carbon atom. The fact that the product of the rearrangement is determined solely by the spatial configuration of the oxime is thus accounted for. The process, whilst requiring —OX to exert a powerful attraction for electrons, should be facilitated by any factor, such as an electron-repelling group on A or B, tending to increase the concentration of electrons at A—C and *vice versa*, and it might also be expected that such substitution should be more effective on A, which participates in the bond A—C, than on the more remote group B. These are precisely the effects that have been observed.



(VIII.)

Such a formulation of the transformation can only be regarded as provisional, but it appears to agree with all the facts available regarding the rearrangement of the ketoximes. It bears a close resemblance to the picture drawn by Mills (British Association Address, *Chem. and Ind.*, 1932, **10**, 755) and differs from it mainly in assigning to the union of the nitrogen atom with group A a more important share in the determination of the ease of rearrangement. Were the rate of change determined solely by the polarisation of the N—O bond or the attraction of —OX for tbe central carbon atom, it would be expected that the effects of substitution in the two groups A and B would be nearly equal instead of being markedly different.

As a result of the work described in this series of papers certain definite general conclusions have been reached regarding the nature of the Beckmann change of ketoximes, and these are now summarised.

1. The rearrangement of oxime esters and related compounds first described by Kuhara is, indeed, a spontaneous transformation brought about by heat alone and not requiring an external reagent, though its velocity depends upon the polar character of the solvent, if any, in which it takes place.

2. There is no evidence that this spontaneous transformation involves any actual dissociation into free ions. Such a dissociation appears inherently improbable, and the change is best regarded as truly intramolecular.

3. The activity of the majority of reagents employed to bring about the Beckmann change in ketoximes can readily be explained by the intermediate formation of an ester-like compound capable of undergoing spontaneous rearrangement. Study of the outstanding example of a reagent that did not appear to fall into this category showed that it, too, acted in the same way, which therefore appears to be the one general mode of transformation.

4. A more detailed mechanism of the change has been suggested which takes into account both the effects of substitution on the ease of rearrangement and the spatial factor which determines the nature of the product of transformation of an unsymmetrical ketoxime.

EXPERIMENTAL.

(Analyses are micro-determinations by Dr. A. Schoeller.)

The picryl ethers of the various oximes were prepared by the method described in Part I. The purity of each of the unsymmetrical oxime derivatives was checked by converting it into the corresponding *N*-picrylanilide, and purification was continued until this could be obtained free from any appreciable trace of isomeride.

Separation of the Stereoisomeric Oximes.—More convenient methods than those in the literature were found for the separation of the two isomeric oximes of *p*-chloro- and *p*-methylbenzophenone. The mixture of *p*-chlorobenzophenoueoximes was crystallised twice from alcohol, and the main yield of α-oxime obtained (m. p. 163—164°). The filtrates were diluted with water, the precipitate being rich in β-oxime. After drying, this was extracted with cold alcohol, which left behind most of the remaining α-oxime. The β-oxime was again precipitated by water, and was recrystallised from light petroleum (b. p. 60—80°). The material so obtained (m. p. 92—95°) was used for preparation of the picryl ether.

The two phenyl tolyl ketoximes had been separated by Hantzsch (*Ber.*, 1890, **23**, 2325) by fractional precipitation with water from solution in glacial acetic acid, but this method is unsatisfactory when the isomerides are required in considerable quantities. It was found that the α-oxime is sparingly soluble in acetone but the β-compound readily so. The isomerides were therefore separated by extraction with acetone, which left a residue of almost pure α-oxime (m. p. after recrystallisation from alcohol 153—156°). The acetone solution was diluted with water, and the extraction and precipitation repeated on the crude β-oxime so obtained. The final precipitate of β-oxime was further purified by crystallisation from light petroleum (m. p. 114—116°). It decomposed even on standing in the open air, and was converted into the picryl ether as soon as purified.

The two oximes of *p*-nitrobenzophenone were obtained by Sutton and Taylor's modification (J., 1931, 2190) of Brady and Mehta's method (J., 1924, **125**, 2297).

The following compounds have not been previously described.

Phenyl p-*tolyl α-ketoxime picryl ether*, colourless minute needles from chloroform and methyl alcohol, m. p. 103° (Found: C, 56·85; H, 3·5. $C_{20}H_{14}O_7N_4$ requires C, 56·85; H, 3·35%). It yielded p-*toluoyl*-N-*picrylanilide*, pale yellow crystals from acetone and alcohol, m. p. 209° (Found: C, 56·7; H, 3·4%), when heated in carbon tetrachloride solution, and this was also prepared from *p*-toluanilide imidochloride and sodium picrate (cf. Mumm, Hesse, and Volquartz, *Ber.*, 1915, **48**, 379).

Phenyl p-*tolyl β-ketoxime picryl ether*, yellowish-brown crystalline powder from acetone and alcohol, m. p. 83° (Found: C, 56·2; H, 3·3%), was converted into *benz*-N-*picryl*-p-*toluidide*, bright yellow crystals, m. p. 180—185° (Found: C, 56·9; H, 3·45%), which was also synthesised from benz-*p*-toluidide imidochloride and sodium picrate. The preparation and crystallisation from chloroform and alcohol of di-*p*-tolyl ketoxime picryl ether, m. p. 95°, were best conducted in a freezing mixture (cf. Part I).

p-*Nitrobenzophenone-α-oxime picryl ether*, pale yellow crystals from acetone and alcohol, m. p. 134° (Found: C, 50·45; H, 2·65. $C_{19}H_{11}O_9N_5$ requires C, 50·3; H, 2·45%), yielded, on hydrolysis with cold alcoholic potash, *p*-nitrobenzophenone-α-oxime (m. p. and mixed m. p.

154—156°). It was converted into p-*nitrobenz*-N-*picrylanilide*, pale yellow plates from acetone and alcohol, m. p. 214—215° (Found : C, 50·45; H, 2·35%), when heated in ethylene dichloride solution (2 g. in 25 c.c.) in a sealed tube at 100° for 5 hours.

p-*Nitrobenzophenone*-β-*oxime picryl ether*, pale brown crystalline powder from acetone and alcohol, m. p. 154—155° (decomp.) (Found : C, 50·65; H, 2·55%), gave the β-oxime (m. p. and mixed m. p. 135—138°) on hydrolysis with cold alcoholic potash. After 6 hours' heating at 100° in ethylene dichloride solution, evaporation of the solvent yielded only unchanged picryl ether (m. p. 140—145°, mixed m. p. 146—148°, m. p. and mixed m. p. after recrystallisation 154—155°).

pp'-*Dinitrobenzophenoneoxime*, almost colourless needles from alcohol, m. p. 195° (decomp.), was obtained by boiling the ketone (10 g.) with hydroxylamine hydrochloride (5 g. in 10 c.c. of water) and alcohol (40 c.c.) for 2 hours (Found : C, 54·3; H, 3·3. $C_{13}H_9O_5N_3$ requires C, 54·3; H, 3·15%).

pp'-*Dinitrobenzophenoneoxime picryl ether*, almost colourless, fine needles from acetone and alcohol, m. p. 189° (decomp.) (Found : C, 45·9; H, 2·1. $C_{19}H_{10}O_{11}N_6$ requires C, 45·8; H, 2·0%). It yielded the oxime (m. p. 189—192°, mixed m. p. 192—193°) when hydrolysed with cold alcoholic sodium hydroxide, but was recovered unchanged after 7 hours' heating at 100° in ethylene dichloride solution (m. p. and mixed m. p. 186°).

Benzophenoneoxime 2 : 4-*dinitrophenyl ether*, colourless fine needles (m. p. 173—174°) from acetone (Found : C, 62·7; H, 3·6. $C_{19}H_{13}O_5N_3$ requires C, 62·8; H, 3·6%), gave benzophenone-oxime on hydrolysis (m. p. and mixed m. p. 143—144°). It was recovered unchanged (m. p. 167—169°) after 7 hours' heating at 100° in ethylene dichloride or in nitromethane solution. The isomeric *benz*-N-2 : 4-*dinitrophenylanilide*, bright yellow crystals from acetone and alcohol, m. p. 155—156° (Found : C, 62·7; H, 3·75%), was obtained from benzanilide imidochloride and sodium 2 : 4-dinitrophenoxide.

p-Chlorobenzophenone-β-oxime picryl ether had m. p. 116—118° (given in Part I as m. p. 109—110°).

When attempts were made to prepare di-*p*-anisyl ketoxime picryl ether from the oxime and picryl chloride, the only substance that could be isolated, even when the reaction was carried out in a freezing mixture, formed colourless plates, m. p. 202—203°, from alcohol, and proved to be *p*-anisoyl-*p*-anisidide (Found : C, 70·0; H, 5·95. Calc. for $C_{15}H_{15}O_3N$: C, 70·0; H, 5·9%), as shown by mixed m. p. with an authentic specimen.

Velocity Determinations.—The method described in Part I for carbon tetrachloride solutions was employed in all measurements except those on the picryl ethers of phenyl tolyl β-ketoxime and di-*p*-tolyl ketoxime, the change products of which were too soluble in this solvent. For these two compounds a somewhat more complicated and less accurate method was adopted as follows : after removal from the thermostat and chilling in ice, each reaction tube was opened and 25 c.c. of the solution were transferred to a 50-c.c. graduated flask and made up to 50 c.c. with ice-cold light petroleum (b. p. 60—80°). The solution was seeded with the appropriate change product, kept in ice for 3 hours with occasional shaking, and then filtered and evaporated as already described.

The results of the measurements are given in the tables below, each value being the mean of six observations. (Concentrations, *c*, are in g.-mol./litre at the particular temperature employed; time in seconds, Napierian logarithms.)

Conversion of benzophenoneoxime picryl ether into benz-N-*picrylanilide*
(values additional to those of Part II).

Temp.					Temp.				
70·4°	c		0·0228		90·7°	c	0·0111	0·0222	0·0333
	$k \times 10^5$		1·80			$k \times 10^6$	15·2	16·8	19·1
80·5	c	0·0112	0·0225	0·0338	100·45	c	0·0109	0·0219	0·0328
	$k \times 10^5$	5·30	6·18	6·48		$k \times 10^5$	40·3	45·1	48·4

Conversion of p-*chlorobenzophenone*-α-*oxime picryl ether into* p-*chlorobenz*-N-*picrylanilide.*

Temp.					
85·8°	c		0·0104	0·0139	0·0208
	$k \times 10^5$		3·88	3·84	3·95
95·0	c	0·0068		0·0136	0·0204
	$k \times 10^5$	9·60		10·4	9·94
99·8	c	0·0067		0·0135	0·0202
	$k \times 10^5$	15·9		17·0	17·3
105·3	c	0·0067	0·0100	0·0134	
	$k \times 10^5$	31·1	31·5	32·3	

Conversion of p-*chlorobenzophenone*-β-*oxime picryl ether into benz*-N-*picryl*-p-*chloroanilide.*

Temp.					Temp.				
90·8°	c		0·0137		104·55°	c	0·0067	0·0134	0·0201
	$k \times 10^5$		2·88			$k \times 10^5$	12·0	12·7	13·2
100·85	c	0·0067	0·0134	0·0202	110·6	c	0·0066	0·0132	0·0199
	$k \times 10^5$	8·41	8·83	9·67		$k \times 10^5$	22·2	23·4	25·0

Conversion of pp′-*dichlorobenzophenoneoxime picryl ether into* p-*chlorobenz*-N-*picryl*-p-*chloroanilide.*

Temp.					
90·8°	c			0·0190	
	$k \times 10^5$			1·56	
100·0	c		0·0094	0·0188	0·0282
	$k \times 10^5$		3·72	4·07	4·58
110·3	c	0·0062	0·0093	0·0185	0·0278
	$k \times 10^5$	12·0	12·7	13·1	13·4
115·5	c		0·0092	0·0183	0·0275
	$k \times 10^5$		19·5	20·8	22·7

Conversion of phenyl p-*tolyl* α-*ketoxime picryl ether into* p-*toluoyl*-N-*picrylanilide.*

Temp.				Temp.			
65·2°	c	0·0074	0·0148	85·6°	c	0·0072	0·0144
	$k \times 10^5$	2·55	2·46		$k \times 10^5$	22·5	27·0
75·6	c	0·0073	0·0146	90·9	c	0·0071	0·0143
	$k \times 10^5$	7·91	8·35		$k \times 10^5$	39·5	46·7

Conversion of phenyl p-*tolyl* β-*ketoxime picryl ether into benz*-N-*picryl*-p-*toluidide.*

Temp.				Temp.			
55·5°	c	0·0090	0·0180	75·3°	c	0·0088	0·0176
	$k \times 10^5$	2·2	2·2		$k \times 10^5$	21	23
65·0	c	0·0089	0·0178	80·4	c	0·0087	0·0174
	$k \times 10^5$	8·6	7·3		$k \times 10^5$	41	45

Conversion of di-p-*tolyl ketoxime picryl ether into* p-*toluoyl*-N-*picryl*-p-*toluidide.*

Temp.					Temp.				
44·7°	c		0·0147		64·6°	c		0·0143	
	$k \times 10^5$		3·0			$k \times 10^5$		32·4	
50·3	c	0·0073	0·0146		70·3	c	0·0071		0·0214
	$k \times 10^5$	7·4	6·2			$k \times 10^5$	59		66
60·4	c	0·0072	0·0144	0·0217					
	$k \times 10^5$	18·1	19·6	19·1					

Conversion of benzophenoneoxime 2 : 4 : 6-*trinitro*-m-*tolyl ether into benz*-N-2 : 4 : 6-*trinitro*-m-*tolylanilide.*

Temp.				Temp.			
89·4°	c		0·0215	102·8°	c	0·0106	0·0211
	$k \times 10^5$		2·40		$k \times 10^5$	12·1	12·2
92·1	c	0·0107	0·0214	104·8	c	0·0105	0·0210
	$k \times 10^5$	3·9	3·95		$k \times 10^5$	15·3	17·0
95·0	c	0·0107	0·0213	108·7	c	0·0105	
	$k \times 10^5$	5·4	5·72		$k \times 10^5$	22·2	
100·1	c	0·0106	0·0212	111·2	c	0·0104	
	$k \times 10^5$	6·80	8·25		$k \times 10^5$	34·3	

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109. *The Kinetics of the Reaction between Hydrogen and Sulphur. Part III.* (i) *Reaction at 350—412° and 50—150 mm.* (ii) *Behaviour of Sulphur on a Hot Glass Surface.*

By Ralph P. Cook and Percy L. Robinson.

(i) Up to 350°, and from a few mm. to 1 atm. of hydrogen, the reaction with sulphur is homogeneous and has a velocity proportional to the concentration of hydrogen and the square root of the concentration of sulphur (Aynsley, Pearson, and Robinson, J., 1935, 58). Below this pressure range, a reaction on the glass is detectable, which, however, ceases immediately it has covered the surface with a unimolecular layer of hydrogen sulphide. At pressures greater than a few mm., the amount of hydrogen sulphide produced heterogeneously, even in packed vessels, is too small for independent recognition (Aynsley and Robinson, J., 1935, 351). The cessation of the heterogeneous reaction was ascribed to the occupation of the surface by molecules of hydrogen sulphide, and it was anticipated that at higher temperatures this layer would be wholly, or in part, desorbed, and a continuous reaction would proceed on the cleared surface. It has been necessary, in connexion with other work shortly to be published, to extend our knowledge of the hydrogen–sulphur reaction up to the highest temperature at which it could be accurately measured, which, unfortunately, was only 412°, on account of the velocities there experienced, but the onset of a continuous heterogeneous reaction has not been observed.

The experimental procedure was similar to that previously described. Over the extended temperature range the velocity remains proportional to the hydrogen concentration (Table I*a*) and to the square root of the sulphur concentration (Table I*b*). The reaction rates over a period of 5 minutes' actual heating were obtained by using two identically charged bulbs, one being heated for 3 and the other for 8 minutes, and taking the difference. The reaction is also independent of the area of the glass surface (Table I*c*).

Table I.

(*a*) *Effect of hydrogen concentration.*

Vol. of bulb = 218 c.c. Weight of sulphur = 0·0534 g. Time of heating = 5 mins. Temp. = 675° Abs.

Press. of hydrogen at 15°, mm.	51	102	153
Rate of H_2S formation, g./c.c./sec. × 10^{10}	398·0	806·5	1199·0
Ratio of rates	1·00	2·03	3·01

(*b*) *Effect of sulphur concentration.*

Vol. of bulb = 218 c.c. Press. of H_2 = 153 mm. (at 15°). Time of heating = 5 mins. Temp. = 675° Abs.

Wt. of sulphur, g.	0·0534	0·1000	0·1500
Rate of H_2S formation, g./c.c./sec. × 10^{10}	1199	1676	2036
(Rate/$\sqrt{[S]}$) × 10^{11}	519·0	530·0	525·6

(*c*) *Effect of glass surface.*

Vol. of bulb, c.c.	Wt. of S, g.	Press. of H_2, mm. (at 15°).	Glass surface, sq. cm.	Abs. temp.	Rate of H_2S formation, g./c.c./sec. × 10^{10}.
218	0·0534	153	175	675°	1199
218	0·0534	153	895	675	1220

Table II, corrected for the fall in concentration of sulphur during the reaction, shows that the plot of the logarithm of velocity against $1/T$ (see fig.) continues the straight line

Table II.

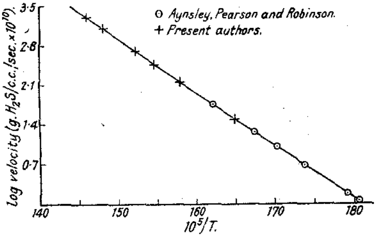
Velocity and temperature.

Vol. of bulb = 218 c.c. Conc. of sulphur = 0·0534/218 g./c.c. Hydrogen press. = 153 mm. (at 15°).

Abs. temp.	606°	633°	647·5°	656·7°	675°	688·1°
Rate of H_2S formation, g./c.c./sec. × 10^{10}	34·1	152·8	335·4	546·8	1199·0	1941·5

given in Part I, Fig. 3, and indicates an identical temperature coefficient (1·9) and heat of activation (43·3 kg.-cals.). Evidently the kinetics of the reaction remains unchanged; in particular, there is no increase in the heterogeneous contribution.

(ii) The observations described in Parts I and II and above are contrary to those which led Norrish and Rideal (J., 1923, **123**, 696) to state that "as a result of experiments carried out using flasks of different internal surface area it was found possible to show that the surface action" (which in their case was believed to be considerable and continuous) "is directly proportional to the area of the internal surface of the reaction chamber, and thus independent of the quantity of sulphur present." They used a flow method and found "that on removing the reaction flask suddenly from the bath, the whole internal surface was covered with a thin film of liquid sulphur which quickly solidified to a coating of feathery crystals." When we first encountered the difficulty of accepting the original work, Dr. Norrish kindly sent us one of his own flasks showing the coating described, and with it we repeated many times the operation of sudden removal from the bath, but were forced to conclude that the liquid film seen by Dr. Norrish arises from the condensation of sulphur vapour upon the walls of the vessel. The distribution of the condensate thereon is changed by any irregularity in cooling: for instance, the sulphur can be made to separate entirely on one side of the flask, by suitably cooling that region, and to leave the other side



quite free. Of more importance than the liquid which separates on cooling, however, is the question whether, as alleged by Norrish and Rideal, a liquid film is present on the glass surface during the time the flask is at the reaction temperature. To investigate this, we have heated sulphur in (i) a stream of hydrogen and (ii) closed vessels with hydrogen and alone, and have used soft, Monax, and Pyrex glasses for these purposes. In the first case, the apparatus was similar to that of Norrish and Rideal (*loc. cit.*) except that the heating liquid, colourless paraffin, was in a large, lagged, Pyrex beaker provided with two narrow windows in the asbestos covering, to serve severally for the illumination and the observation of the reaction vessels and their contents.

The flask, through which hydrogen was passing, was submerged in the bath so slowly that the whole surface was successively covered with liquid sulphur which, evaporating from the bottom, condensed just above the level of the bath liquid. At the temperatures employed, 260—310°, the sulphur at the bottom of the flask failed to wet the glass, with which it assumed a contact similar to that shown by mercury and other non-wetting liquids. The lower edge of the ring of liquid adhering to the neck, where it was but little below bath-temperature, presented a like contact. Between the pool in the bottom and the material in the neck, the glass was free from a visible film, the presence of which could have been readily recognised because, unlike the liquid, sulphur vapour is, even at these temperatures, light in colour. After a time, sulphur collected to such an extent in the neck that it flowed down as pensile drops which, in their passage, did not spread out over the glass, and left upon the surface narrow, dark brown smears that became fainter by evaporation, broke into small globules, and finally disappeared. These smears served to indicate the dark

colour which a liquid film such as that postulated by Norrish and Rideal would assume at these temperatures and thereby render itself readily recognisable if present.

Closed vessels, containing sulphur either in a vacuum or with hydrogen, slowly lowered into the bath so that their surfaces were successively covered with liquid showed no evidence of a liquid film when equilibrium was reached, the whole of the sulphur being then in a pool at the bottom.

Neither long periods of maturing at the working temperatures, nor changes in the type of glass affected this behaviour.

These observations bear out our previous conclusion that glass is not "wetted" by sulphur at these temperatures, a view which has gained further support by the recent work of Sayce (J., 1935, 1767) on the kinetics of the oxidation of sulphur.

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110. *Studies in Graphite Formation. Part II. The Chemical Nature of Graphite and Amorphous Carbon.*

By A. E. BALFOUR, H. L. RILEY, and R. MORRIS ROBINSON.

CARBON with an electrical conductivity almost equal to that of Ceylon graphite is obtained when hexaiodobenzene is decomposed at 770° (Ciusa, *Gazzetta*, 1928, **58**, 222), a temperature at which carbonaceous substances containing hydrogen yield carbon of relatively high specific resistance. Hofmann and Frenzel (*Ber.*, 1930, **63**, 1248) have shown that carbon deposited on iron from carbon monoxide gives an 83·3% yield of graphitic oxide when subjected to Brodie's reaction, whereas carbon from petroleum soot gives only a 20·2% yield. It is well known (cf., *inter alia*, Burgess and Wheeler, J., 1910, **97**, 1917; Stock, Lux, and Rayner, *Z. anorg. Chem.*, 1931, **195**, 158) that the volatile matter evolved in the carbonisation of substances such as coal, at temperatures above 700°, is principally hydrogen. These facts, and others given below, indicate that in the formation of carbon, by the pyrolysis of carbonaceous material, the presence of hydrogen plays a very important part.

It has been assumed by many workers that amorphous carbon consists of very small crystals of graphite more or less contaminated with complex hydrocarbons. This assumption is only partly true, for it is shown here, on both theoretical and experimental grounds, that small quantities of hydrogen play a fundamental part in modifying the properties of the graphite crystal lattice.

Adam (*Trans. Faraday Soc.*, 1934, **30**, 57) pointed out that if we fix our attention on one of the carbon atoms in a hexagon plane of the graphite lattice, it becomes apparent that its three valency bonds lead to three aromatic hexagons, suggesting a similarity, "though this may be only superficial," between the structure of graphite and of triphenylmethyl. A comparison of the properties of graphite with those of the triarylmethyls leaves little doubt that this formal similarity is reflected in a very fundamental way in the chemical properties of these substances.

The presence of three aromatic radicals attached to the same carbon atom brings about a pronounced modification in the properties of the fourth valency (cf. *inter alia*, Ingold, *Ann. Reports*, 1928, **25**, 150); for instance, (*a*) hexaphenylethane dissociates into free radicals in non-ionising solvents and into both positive and negative triphenylmethyl ions in ionising solvents; (*b*) triphenylmethyl chloride gives, in liquid sulphur dioxide, a conducting solution which contains the ions Ph_3C^+ and Cl^-; (*c*) triphenylmethyl forms compounds with the alkali metals which dissociate in liquid ammonia forming positive alkali-metal ions and negative triphenylmethyl ions; (*d*) triphenylmethane acts as a weak acid; (*e*) hexaphenylethane takes up oxygen from the atmosphere spontaneously to form a peroxide. Each of these fundamental properties can be paralleled closely from the chemistry of graphite. (*a*) The crystal structure and chemical properties of graphite

(*vide infra*) indicate that each hexagon plane can act as a macro-free radical. It is of interest that polynuclear aromatic systems act more powerfully than phenyl in promoting the dissociation of hexa-arylethanes (cf., *inter alia*, Ingold, *loc. cit.*). (*b*) Frenzel and Hofmann (*Z. Elektrochem.*, 1934, **40**, 511) prepared graphite bisulphate in which the carbon hexagon planes remained intact, the hydrogen sulphate ions having penetrated between them, increasing their distance apart. Ruff and Bretschneider's graphite monofluoride (*Z. anorg. Chem.*, 1934, **217**, 1) is a similar type of compound, though much more stable. In these compounds, the hexagon planes are playing the part of macro-positive radicals. (*c*) Fredenhagen and Cadenbach (*Z. anorg. Chem.*, 1927, **158**, 249) and Fredenhagen and Suck (*ibid.*, 1929, **178**, 353) have prepared the compounds C_8K and $C_{16}K$, and Schleede and Wellmann (*Z. physikal. Chem.*, 1932, *B*, **18**, 1) have shown that in these compounds the alkali-metal atoms had penetrated and formed layers between the hexagon carbon planes. These compounds are obviously analogous to the alkali-metal triphenylmethides, and the hexagon planes are acting as macro-negative radicals. (*d*) Lengyel (*ibid.*, 1931, **154**, 371) has shown that the potential of a graphite electrode is determined by the p_H of the solution and is not influenced by the pressure of gaseous hydrogen surrounding the electrode. Bangham and Stafford (J., 1925, **127**, 1085) found that graphite will adsorb hydrogen ions, but not molecular hydrogen, from the gas phase. These phenomena indicate that graphite possesses a definite affinity for hydrogen ions. (*e*) The nature of graphitic oxide has recently been studied in detail by Hofmann and Frenzel and their collaborators (*Ber.*, 1930, **63**, 1248; *Z. Elektrochem.*, 1931, **37**, 613; *Kolloid Z.*, 1932, **58**, 7; *Annalen*, 1934, **510**, 1) and by Thiele (*Z. Elektrochem.*, 1934, **40**, 26). Hofmann and his co-workers deduce from their *X*-ray studies that the oxygen atoms in graphitic oxide, of empirical formula C_3O, are attached to the carbon atoms in the planes by an ethylene-oxide type of linkage. In view of the aromatic character of the hexagon planes, it is more probable that the oxygen is peroxidic in character. Such a view is not contrary to the experimental results of the above workers and is in accord with the explosive property of graphitic oxide and with the fact that, when shaken with water (or certain organic liquids), it is completely dispersed into micelles possessing only single hexagon layers (Kohlschütter and Haenni, *Z. anorg. Chem.*, 1919, **105**, 121). The swelling of graphitic oxide in water and its final dispersion is, on the above view, a dissociation of the graphitic peroxide into macro-free radicals or ions brought about by the fission of the weakened —O—O— bond. The 8% of water remaining in the oxide even after prolonged drying, which has been shown by Hofmann and his co-workers to be present as H_2O molecules, is probably there as solvated water. This view of the peroxidic character of graphitic oxide brings its properties into line with the general properties of aromatic peroxides (Goldschmidt and Steigerwald, *Annalen*, 1924, **438**, 202) and of the ketyls, and it also indicates that graphitic oxide is the analogue of Gomberg's hexaphenylethane peroxide. That graphite does not take up oxygen in a manner similar to hexaphenylethane is possibly connected with the size of the graphite crystallites, which probably determines the magnitude of the energy barrier to the penetration of oxygen molecules between the hexagon planes. Acheson graphite does not sorb molecular oxygen, but active carbons have been prepared which, after sorbing oxygen, exploded on heating (Ruff and Bretschneider, *loc. cit.*), a behaviour reminiscent of graphitic oxide (see also Meyer, *Z. physikal. Chem.*, 1932, *B*, **17**, 385; Berl, Andress, Rheinhardt, and Herbert, *ibid.*, 1932, *A*, **158**, 273).

The above considerations leave no doubt as to the pronounced aromatic character of the carbon hexagon planes in pure graphite. Their striking stability is a consequence of the large number of resonance forms in which the planes can exist. The amphoteric character of the planes suggests the possibility of the existence of inter-planar resonance forms. At the inter-planar distance of 3·4 Å., ordinary valency forces would be very weak. The general stability of graphite crystals [cf. coronene (hexabenzobenzene, Scholl and Meyer, *Ber.*, 1932, **65**, 902), which sublimes in vacuum at 500°] suggests that more than van der Waals forces are involved in the bonding of the planes together (cf. Lennard-Jones, *Trans. Faraday Soc.*, 1934, **30**, 58; Hückel, *ibid.*). There can, however, be little doubt that inter-planar resonance is concerned in the bonding of foreign atoms and radicals between the planes, because of the curious, step-wise manner in which the potassium

graphite compound, C_8K, and graphite bisulphate decompose. Schleede and Wellmann (*loc. cit.*) showed that when C_8K was decomposed by heating, alternate layers of potassium atoms were expelled to form $C_{16}K$. Graphite bisulphate decomposes on hydrolysis in a somewhat similar step-wise manner (Frenzel and Hofmann, *Z. Elektrochem.*, 1934, **40**, 511).

The relatively high stability of graphite monofluoride and the great tautomeric activity of hydrogen suggest that the graphite crystal lattice will be capable of bonding atoms of hydrogen between the hexagon planes in a very stable manner, and, further, that the presence of relatively small amounts of hydrogen ($< 1\%$, cf. the compounds C_8K and $C_{16}K$) will have a very pronounced effect upon the properties of the carbon.

Those types of carbon usually referred to as "amorphous" all contain appreciable quantities of hydrogen. The above theory of the inter-planar bonding of this hydrogen offers a simple explanation as to why these carbons differ so pronouncedly in chemical and physical properties from pure graphitic carbon. The high stability of the hexagon planes in pure graphite is due to their aromatic character. The inter-planar bonding of hydrogen must reduce the stability of the hexagon planes, because the fourth valencies of some of the carbon atoms are brought into play, and this will reduce the number of resonance forms in which the planes can exist. There will, of course, be a corresponding increase in the number of inter-planar resonance forms; *i.e.*, the presence of tautomeric hydrogen between the planes reduces their aromatic character, with consequences illustrated by the following examples.

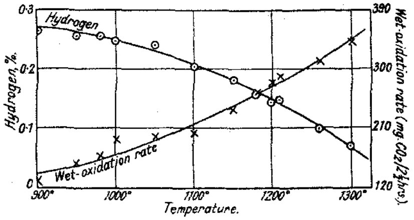
Pure graphite gives excellent yields of graphitic oxide when subjected to Brodie's reaction, whereas most of the so-called amorphous carbons give very poor yields or none at all. This difference in behaviour is no doubt due to the more stable aromatic hexagon planes in graphite withstanding the action of the oxidising solution more successfully than the less stable, more aliphatic planes in "amorphous" carbon. The latter is much more reactive to gaseous oxygen below 1000° than is graphite; there is considerable evidence to indicate that the reverse state of affairs exists at higher temperatures. The above theory readily accounts for this: the less stable nature of the hexagon planes in "amorphous" carbon permits of their edge-wise combustion, whereas with graphite rapid combustion will only occur when the oxygen can penetrate freely between the planes, *i.e.*, at high temperatures (cf. Meyer, *loc. cit.*). Ruff and Bretschneider (*loc. cit.*) have shown that carbon burns in fluorine in two ways, *viz.*, (a) by a smooth reaction yielding volatile carbon fluorides, and (b) explosively, through the intermediate formation of the solid compound, graphite monofluoride, in which the fluorine atoms are bonded between the hexagon planes.

The above considerations indicate that the hexagon planes of graphite can act as macro-free radicals, and it is therefore probable that the paramagnetic nature of oxygen is an important factor in the combustion of graphite. It is significant, in this connexion, that chlorine dioxide, which contains an odd number of electrons, is the reagent most generally employed in the preparation of graphitic oxide.

In order to obtain still further confirmation of the above views as to the importance of small amounts of hydrogen in determining the properties of carbon, a large bulk sample of sugar charcoal was prepared at approximately 900°, and small samples of this were heated in vacuum for 3 hours at a series of temperatures above 900°. The hydrogen content, the susceptibility to oxidation by the chromic–phosphoric solution (Blayden and Riley, *J. Soc. Chem. Ind.*, 1935, **54**, 159T; Balfour and Riley, J., 1935, 1723), and the specific resistance of the resulting carbons were determined. Hydrogen content and wet-oxidation rate are plotted against temperature in Fig. 1. The complementary nature of these two curves is obvious. The slope of the wet-oxidation curve indicated that a specimen of carbon, free from hydrogen, would react very rapidly, possibly explosively, with the solution of chromic acid in phosphoric acid. This proved to be the case when a sample of kish (carbon which had crystallised from molten pig iron) was subjected to this test. During the first 20 minutes of the test, carbon dioxide was evolved from a graded 1-g. sample at the rate of 3,000 mg. per 2½ hrs., then the remaining carbon suddenly swelled up rapidly, completely filling the reaction vessel (approximately 150 c.c.), probably owing to the formation of graphitic oxide or some similar compound. This result is interesting in view of Thiele's

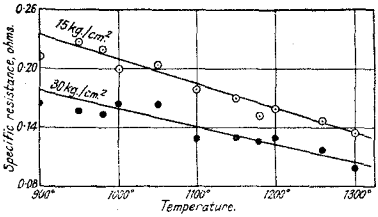
statement (*loc. cit.*) that graphite does not swell when anodically polarised in syrupy phosphoric acid, whereas swelling occurs in concentrated sulphuric and nitric acids.

Fig. 1.



These curves, and those of the specific electrical resistance of the samples of carbon under two external pressures (Fig. 2), show that decrease in hydrogen content is accompanied by an increase in the wet-oxidation rate and the electrical conductivity, *i.e.*, an increase in the graphite content of the samples.

Fig. 2.



Experiments in which the carbon samples were heated in a vacuum for different periods indicated that after 3 hours either the hydrogen content had reached an equilibrium value or only a very slow elimination of hydrogen occurred after this period. The following results were obtained.

Temp.	Time of heating, hrs.	H, %.	Wet-oxidation rate (mg. CO_2/2½ hrs.).	Temp.	Time of heating, hrs.	H, %.	Wet-oxidation rate (mg. CO_2/2½ hrs.).
1000°	3	0·249	194	1200°	1·5	0·163	242
	6	0·232	198		3	0·133	279
					6	0·142	274

A factor involved in determining the extent of graphitisation and the size of the graphite crystallites produced when an organic compound is carbonised, is the chemical nature of the compound employed. Another factor is obviously the speed of carbonisation. Before hydrogen can be stably bonded in the carbon lattice, the establishment of some arrangement approximating to the hexagon planes of graphite is necessary. This will occupy an appreciable time, for it involves the interaction of a large number of carbon atoms. The escape of hydrogen from the solid phase probably depends upon the formation of molecular hydrogen or simple hydrocarbons, involving the interaction of only a small number of atoms. Rapid carbonisation, therefore, will increase the probability of the escape of hydrogen, as less time will be available for the formation of the hexagon layer structure. Consequently, rapid carbonisation should yield a more highly graphitised

carbon. To test this view, two cokes A and B were prepared by carbonising two samples of the same coal in a nitrogen-filled electric furnace, A being placed in a furnace already at 900° and kept there for an hour; and B being put into a cold furnace, heated at the rate of 3° a minute to 900°, and kept at this temperature for one hour. Examination of the resulting cokes gave the following results.

	H, %.	Wet-oxidation rate (mg. CO_2/2½ hrs.).
Coke A (rapid carbonisation)	0·58	180
Coke B (slow carbonisation)	0·89	106

The effect of rate of carbonisation upon the graphite content of the resulting cokes is further illustrated by Fig. 3, in which maximum carbonising temperature is plotted against wet-oxidation rate. The continuous curve shows the results obtained on rapidly coking a Northumberland coal at different temperatures, and the broken line those when the same

Fig. 3.

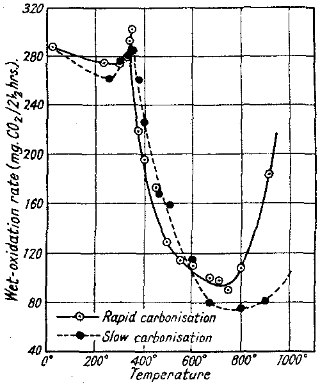
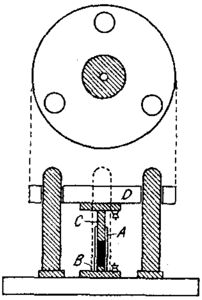


Fig. 4.



coal was carbonised slowly, *i.e.*, being heated at the rate of 5° a minute up to the various temperatures shown. The relative position of the two curves at temperatures above 650° indicates that rapid carbonisation produced the more highly graphitised coke. The curves in Fig. 3 are typical of a large number which have been obtained from the study of various coals. The form of these curves has been discussed in Part I (*loc. cit.*).

The above theoretical considerations and experimental results leave little doubt as to the fundamentally important part which hydrogen plays in the transformation of an organic compound into elementary carbon. Many of the substances usually termed " amorphous carbon " are compounds possessing a crystal lattice similar to that of graphite, with hydrogen firmly bonded between the hexagon planes. The curves shown in Fig. 3 and in Fig. 4 of Part I (*loc. cit.*) indicate that this carbon–hydrogen compound possesses considerable stability and commences to decompose only between 600° and 700°. The actual temperature is probably determined to some extent by the size of the crystallites present in the sample. The work of Berl, Andress, Rheinhardt, and Herbert (*loc. cit.*), Hofmann and Wilm (*ibid.*, 1932, **18**, 401), and Arndt and Pollack (*Z. anorg. Chem.*, 1931, **201**, 81) appears to indicate that the presence of hydrogen has only a small effect upon the distance apart of the hexagon planes of the graphite lattice, for many of the samples of carbon examined by those workers undoubtedly contained appreciable quantities of hydrogen (cf. Hofmann and Groll, *Ber.*, 1932, *B*, **65**, 1257). It is possible that the inter-

planar bonding of hydrogen gives rise to the "mesomorphic state" suggested by Berl and co-workers (*loc. cit.*). Crystallite growth and the presence of hydrogen are probably intimately connected at temperatures below 1300° (see Wesselowski and Pertzow, *Z. anorg. Chem.*, **1934**, **216**, 228, and Arndt and Pollack, *loc. cit.*, for studies of graphitisation at higher temperatures), and the disregard of the fundamental importance of the presence of small traces of hydrogen renders the interpretation of *X*-ray data, with reference to the size of the crystallites, uncertain.

Further evidence in support of the existence of a stable carbon–hydrogen compound is provided by the fact that anthracite and not graphite is apparently the end point in the process of coal formation. Apart from the relatively rare occurrence of igneous intrusions, it is generally agreed that coal deposits have not been subjected to temperatures much above the normal, *i.e.*, in the course of geological time the coal has not been subjected to a temperature sufficiently high to bring about the decomposition of the stable carbon–hydrogen compound (cf. Weinschenk, *Abh. Bayr. Akad.*, 1900, **21**, 233, quoted by Kohlschütter, *Z. anorg. Chem.*, 1919, **105**, 35).

Experimental.

A large stock sample of sugar charcoal was prepared by carbonising successive quantities of sucrose in an electrically heated muffle furnace for about 6 hours at approximately 900°. The product was crushed and sieved on a 20 I.M.M. sieve, the more finely divided product being returned to the muffle with the next charge. The whole sample was thoroughly mixed. About 10 g. of this stock sample were placed in a silica test-tube and heated for 3 hours in vacuum (0·01 mm.) in an electrically heated tube furnace. The carbon was allowed to cool in a dry atmosphere, and its hydrogen content determined by the combustion of a 2-g. sample, blank combustions being performed at frequent intervals in order that the results could be corrected accurately. The percentages of hydrogen were calculated on an ash-free basis, the sugar charcoal containing approximately 4% of ash. All the experiments were carried out in duplicate, and results were obtained over the range 900—1300°. The wet-oxidation rate of each sample was determined as described by Blayden and Riley (*loc. cit.*).

The specific resistances of the various specimens of carbon were determined by means of the apparatus shown in Fig. 4. A few grams of the sample, graded between 60 and 100 I.M.M. sieves, were dried in vacuum at 300° immediately before the determination. A thin layer of the carbon was placed in the thick-walled glass tube, *A*, resting on the cylindrical brass electrode, *B*, which fitted closely inside the glass tube. Another cylindrical brass electrode, *C*, of the same diameter, was placed in position, and a suitable weight placed on the platform *D*. The latter was tapped gently until the resistance of the column of carbon, as measured by a Wheatstone's bridge, became constant. The distance between the contact ends of the two electrodes was measured by means of a cathetometer. The height of the column of sugar charcoal was increased by the addition of a further quantity of the sample, and the resistance was measured in a similar manner. This procedure was repeated until the length of the column was approximately 2 cm. The length and the resistance of the first column of sugar charcoal were subtracted from subsequent readings, to eliminate end effects, and the mean specific resistance was calculated. Further measurements were made with a higher pressure. The original bulk sample of sugar charcoal had a hydrogen content of 0·273%, a wet-oxidation rate of 146 mg. $CO_2/2\frac{1}{2}$ hrs., and a specific resistance of 0·24 ohm at 15 kg./cm.^{2} and 0·20 ohm at 30 kg./cm.^{2}.

The rapid and slow carbonisations were carried out in the electrical furnace described in Part I (Balfour and Riley, *loc. cit.*). The Northumberland coal employed in these experiments had the following composition: ash, 3·9; moisture, 5·4; volatile matter (less moisture), 36·0; C, 82·9; H, 5·4; N, 1·7; S, 2·1; O, 7·9%.

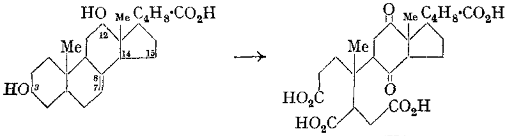
One of us (R. M. R.) is indebted to the Research Council of the British Iron and Steel Federation for a maintenance grant. Our thanks are also due to the Research Committee of Armstrong College for a grant, and to the Northern Coke Research Committee, in whose laboratory this work was carried out, for permission to publish it.

Armstrong College (University of Durham),
Newcastle-upon-Tyne. [*Received, January 6th, 1936.*]

111. *The Action of Selenium Dioxide on Sterols and Bile Acids. Part II. The Formation of Isomeric Dihydroxycholadienic Acids from* apo*Cholic Acid and Dihydroxycholenic Acid and a Note on the Oxidation Products of Dihydroergosterol.*

By R. K. Callow.

The dehydration of cholic acid by zinc chloride in acetic acid yields a mixture of two isomeric acids, $C_{24}H_{38}O_4$, dihydroxycholenic acid and *apo*cholic acid (Boedecker, *Ber.*, 1920, **53**, 1852; Boedecker and Volk, *Ber.*, 1921, **54**, 2489). Dihydroxycholenic acid is catalytically reduced to deoxycholic acid (Boedecker and Volk, *Ber.*, 1922, **55**, 2302), and its oxidative degradation (Borsche and Todd, *Z. physiol. Chem.*, 1931, **197**, 173; Wieland and Dane, *ibid.*, 1932, **206**, 243; **212**, 263) yields a diketo-tetracarboxylic acid, $C_{24}H_{34}O_{10}$. This degradation was interpreted by formulæ (I) and (II), on the assumption that the original acid was 3 : 12-dihydroxy-$\Delta^{7:8}$-cholenic acid (I), though a $\Delta^{14:15}$-acid also would give a diketo-tetracarboxylic acid.



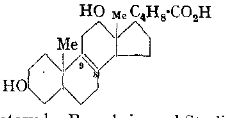
(I.) (II.)

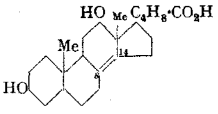
*apo*Cholic acid is not affected by catalytic hydrogenation, but its close relation to dihydroxycholenic acid followed from the observation of Boedecker and Volk (*Ber.*, 1922, **55**, 2302) that either acid, when treated with bromine, was dehydrogenated (by the loss of hydrogen bromide from the dibromide) to give dihydroxycholadienic acids, m. p. 247°, $[\alpha]_D$ + 20·3° and 19·6° in alcohol, respectively, which were reduced catalytically to *apo*cholic acids (acetic acid compounds, $[\alpha]_D$ + 55·9° and + 52·04° in alcohol, respectively; acetic acid compound of original *apo*cholic acid, $[\alpha]_D$ + 45·35°). These results were fully confirmed by Wieland and Deulofeu (*Z. physiol. Chem.*, 1931, **198**, 127), who, however, thought that the discrepancy between the optical rotations was worth noting, and found that the product giving the acetic acid compound of $[\alpha]_D$ + 52°, which they named β-*apo*cholic acid, yielded a dihydroxycholadienic acid of $[\alpha]_D$ − 1°. Dihydroxycholadienic acid can also be obtained by oxidation of *apo*cholic acid with permanganate, or with perbenzoic acid, or by decomposition of *apo*cholic acid oxide, or by oxidation of dihydroxycholenic acid with perbenzoic acid (Borsche and Todd, *Z. physiol. Chem.*, 1931, **197**, 173). No attention was paid in the last investigation to optical rotations, either of the dihydroxycholadienic acids or of the *apo*cholic acids derived from them, and the assumptions of identity were based solely upon melting points. Wieland and Deulofeu (*loc. cit.*) also obtained dihydroxycholadienic acid from *apo*cholic acid and perbenzoic acid, and by hydrolysis of dihydroxycholenic acid oxide (cf. Wieland and Dane, *Z. physiol. Chem.*, 1932, **206**, 243). Wieland and Dane (*ibid.*, 1932, **212**, 263) attempted to determine the position of the ethylenic linkage in *apo*cholanic acid by the oxidation methods which had been applied to dihydroxycholenic acid. The product of oxidation by permanganate was a monocarboxylic acid, having the composition of a diketonic compound, consistent with either of the formulæ (III) and (IV) for *apo*cholic acid. The former was preferred, on account of an analogy with the formation of $\Delta^{9:10}$-octalin from α-decalol, although the oxidation product in this case would, presumably, be a compound with a ten-membered ring.

A third isomeric acid, *iso*dihydroxycholenic acid, was isolated by Yamasaki (*Z. physiol. Chem.*, 1933, **220**, 42) from the product of treatment of cholic acid with hydrochloric acid. It was also obtained hy isomerisation of *apo*cholic acid with hydrochloric acid. To this isomeride, which was not reducible catalytically, Yamasaki assigned the available constitu-

tion (IV). Later (*ibid.*, **1935**, **233**, 10) he demonstrated the interconvertibility of *apo*cholic and dihydroxycholenic acids under the influence of hydrogen chloride (cf. unpublished work

(III.)



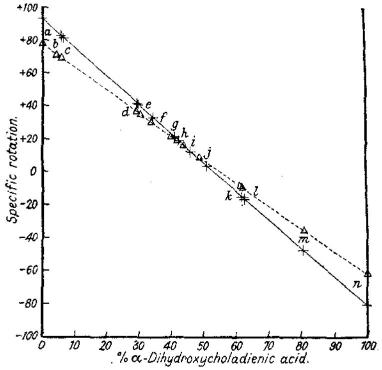


(IV.)

in this laboratory by Rosenheim and Starling, referred to by Rosenheim and King, *Chem. and Ind.*, 1932, 954).

The present investigation is a continuation of the work described in Part I on the oxidation of steroids by selenium dioxide (Callow and Rosenheim, J., 1933, 387). It was

Fig. 1.



Optical rotation and assumed composition of mixtures of α- and β-dihydroxycholadienic acids.

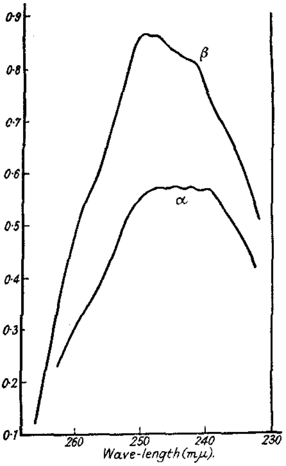
Δ $[\alpha]_D$; + $[\alpha]_{5461}$.

Source of acid: a, β-apo*Cholic acid* + *selenium dioxide.* b, c, apo*Cholic acid* + *selenium dioxide.* d, β-apo*Cholic acid* + *perbenzoic acid.* e, *Decomposition of dihydroxycholenic acid oxide.* f, *Decomposition of* apo*cholic acid oxide.* g, *Methyl dihydroxycholenate* + *selenium dioxide.* h, *Acid from Dr. Boedecker.* i, *Methyl dihydroxycholenate* + *perbenzoic acid.* j, *Methyl dihydroxycholenate* + *selenium dioxide.* k, apo*Cholic acid* + *bromine.* l, *Dihydroxycholenic acid* + *bromine.* m, apo*Cholic acid* + *perbenzoic acid, prep.* (b). n, apo*Cholic acid* + *perbenzoic acid, prep.* (a).

found that *apo*cholic acid reacted readily with selenium dioxide in aqueous-alcoholic solution to give a product having the composition of dihydroxycholadienic acid and not depressing the melting point of an authentic specimen kindly sent by Dr. Boedecker. The new acid, however, had $[\alpha]_D$ +71·0° and $[\alpha]_{5461}$ +82·1° in alcohol, and Dr. Boedecker's acid, in accord with published data, had $[\alpha]_D$ + 18·9° and $[\alpha]_{5461}$ + 19·5°. Since figures for the optical rotation of "dihydroxycholadienic acids" prepared by other methods were not available, a number of these preparations were repeated. A highly lævorotatory acid, $[\alpha]_D$ − 62° and $[\alpha]_{5461}$ − 81°, was obtained from *apo*cholic acid and perbenzoic acid by the method of Borsche and Todd (*loc. cit.*). On the other hand, *apo*cholic acid oxide, formed in the same reaction, decomposed to give an acid with $[\alpha]_D$ + 30° and $[\alpha]_{5461}$ + 33°. Optical rotations between those of the two extreme lævo- and dextro-rotatory acids were observed for the acids prepared from *apo*cholic acid and perbenzoic acid by the method of Wieland and Deulofeu (*loc. cit.*), from *apo*cholic acid and bromine, from dihydroxy-

cholenic acid and bromine, from methyl dihydroxycholenate and perbenzoic acid or selenium dioxide, and from the decomposition of dihydroxycholenic acid oxide. It being assumed that these extremes corresponded to pure lævo- and pure dextrorotatory acid (which it is proposed to call α- and β-*dihydroxycholadienic acid*, respectively), a graph was constructed showing the theoretical rotations of mixtures of these two acids, which will lie along the straight lines joining the values of $[\alpha]_D$ and $[\alpha]_{5461}$ for 100% α-acid and 100% β-acid (Fig. 1). (The values $[\alpha]_D + 77{\cdot}7°$ and $[\alpha]_{5461} + 92{\cdot}8°$ are taken for the β-acid; see below.) If the values of $[\alpha]_D$ and $[\alpha]_{5461}$ for other products are plotted on these lines, the compositions will be indicated by the abscissæ, and if the points for $[\alpha]_D$ and $[\alpha]_{5461}$ for a given product fall one above the other at the same composition, evidence will be afforded that the product is a mixture of α- and β-dihydroxycholadienic acid. Actually, there are small discrepancies, particularly for the products from methyl dihydroxycholenate. These may be accounted for by the difficulty of purifying the materials from unchanged dihydroxycholenic acid. A further check on the assumptions which have been made is afforded by plotting the values of α_{5461}/α_D against composition. The value of this ratio is of the order of 1·2 for steroids. From the value 1·20 for the β-acid it falls through 1·00 at 47% β-acid, to $-\infty$, and the curve reappears at the top of the diagram to fall to 1·33 for the α-acid. It would therefore seem that the latter is not pure, and that the pure α-acid is yet more highly lævorotatory. The determination of the rotatory dispersion, in cases of this kind, can afford valuable evidence as to homogeneity.

FIG. 2.



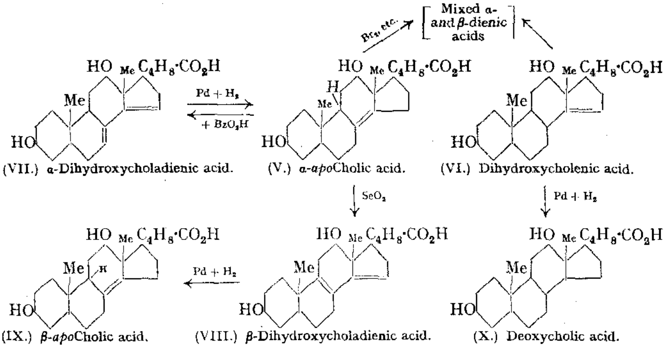
Absorption spectra of α- and β-dihydroxycholadienic acids in alcoholic solution (0·002%).

The two dihydroxycholadienic acids have different absorption spectra (Fig. 2). The curve for the β-acid shows a fairly sharp maximum at 249 mμ, but that for the α-acid is much lower and shows a broad maximum between 240 mμ and 250 mμ. Absorption curves of intermediate type are given by materials which are assumed to be mixtures of these two acids, and there is a fair correlation between the absorption and the composition deduced from the optical activity.

Both α- and β-dihydroxycholadienic acid take up one molecule only of hydrogen when catalytically reduced. The α-acid yields *apo*cholic acid, the acetic acid compound of which has $[\alpha]_D + 42{\cdot}3°$, in fair agreement with the value, $+ 45{\cdot}35°$, given by Boedecker (*loc. cit.*). The β-acid yields an isomeride of *apo*cholic acid, which it is proposed to call β-*apocholic acid*. β-*apo*Cholic acid and its acetic acid and xylene compounds melt at slightly lower temperatures than the α-compounds; the optical rotation, $[\alpha]_D + 73{\cdot}5°$, is considerably higher than that of the known *apo*cholic acid. It would appear that the material which Wieland and Deulofeu called β-*apo*cholic acid was a mixture of the ordinary α-isomeride and the β-acid now described. β-*apo*Cholic acid reacted with selenium dioxide to give a β-dihydroxycholadienic acid with high dextrorotation. With perbenzoic acid a mixture containing a relatively high proportion of β-dihydroxycholadienic acid was obtained. Adam, Askew, and Danielli (*Biochem. J.*, 1935, **29**, 1799) examined surface films of α- and β-*apo*cholic acid and found that they formed gaseous films with identical surface pressure and surface potential, indicating that the isomerism does not involve any serious change in the orientation of the polar groups relative to the ring system.

The interpretation of these reactions makes it necessary to reconsider the formulæ

ascribed to dihydroxycholenic and *apo*cholic acids. Rosenheim and King (*Chem. and Ind.*, 1932, 464, 954) and Morrison and Simpson (J., 1932, 1710) have stressed the analogy between α- and β-ergostenol and *apo*cholic and dihydroxycholenic acid. With the further work of Achtermann (*Z. physiol. Chem.*, 1934, **225**, 141) and of Laucht (*ibid.*, 1935, **237**, 236) on the constitution of $\alpha(\Delta^{8:14})$-ergostenol and $\beta(\Delta^{14:15})$-ergostenol, more certain data are now available, and our knowledge of the ergostenol group can be applied to the acids. The formula proposed by Wieland and Dane (*loc. cit.*) for dihydroxycholenic acid with the ethylenic linkage at positions 7 : 8 is similar to the formula for γ-ergostenol, but the latter substance (Windaus and Langer, *Annalen*, 1933, **508**, 105) is isomerised by finely divided platinum to α-ergostenol, which is not reducible. Since dihydroxycholenic acid is reduced normally to deoxycholic acid, it is better that the $\Delta^{14:15}$-constitution (VI), analogous to that of β-ergostenol, should be assigned to it; the behaviour on oxidation can, as we have seen, be reconciled with this. Further, the direct interconvertibility of dihydroxycholenic and *apo*cholic acid suggests for the latter the $\Delta^{8:14}$-constitution (V), which is also in accord with other evidence. The relations of the isomeric dihydroxycholenic and dihydroxycholadienic acids can then be formulated :

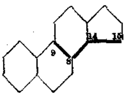


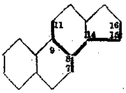
(VII.) α-Dihydroxycholadienic acid. (V.) α-*apo*Cholic acid. (VI.) Dihydroxycholenic acid.

(IX.) β-*apo*Cholic acid. (VIII.) β-Dihydroxycholadienic acid. (X.) Deoxycholic acid.

These formulæ are supported by the following considerations. The methods of formation of α- and β-dihydroxycholadienic acid indicate that they contain conjugated ethylenic in kages. The marked selective absorption in the ultra-violet region confirms the existence of conjugation, and the fact that the absorption of the β-acid is greater and at a longer wave-length than that of the α-acid suggests that in the β-acid there is an enhancing factor such as proximity of a hydroxyl group or presence of the two ethylenic linkages in the same ring. Both acids reacted rather slowly with maleic anhydride in boiling xylene, but no characterisable products could be separated.

On the assumption that the singly unsaturated acids may contain the ethylenic linkage in positions 8 : 9, 8 : 14, or 14 : 15, as shown by the heavy lines in (XI), the doubly unsaturated acids may conceivably contain the ethylenic linkages in the positions shown by heavy lines in (XII). It is possible to eliminate some of the possible formulæ on more or

(XI.) 

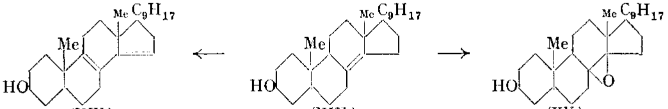


(XII.)

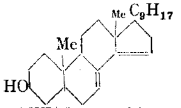
less convincing grounds. The presence of ethylenic linkages at positions 11 : 9-8 : 14, in the same ring as the 12-hydroxyl group, would certainly lead to high absorption at a

longer wave-length than is actually observed. It may even be doubted whether 7 : 8- 9 : 11 ethylenic linkages are admissible, but direct evidence on this point is lacking. On chemical grounds the mechanism of the formation of an ethylenic linkage at positions 15 : 16 presents difficulties. If these restrictions are accepted, we are limited to the formulæ (VII) and (VIII) for the two dihydroxycholadienic acids. Of these two structures, the $\Delta^{9:8\text{-}14:15}$-compound, with two ethylenic linkages in adjacent rings, will be expected to have the higher absorption at longer wave-lengths, and this structure is therefore assigned to β-dihydroxycholadienic acid. Further, the formation of a stereoisomeric *apo*cholic acid from β-dihydroxycholadienic acid, but not from α-dihydroxycholadienic acid, is simply explained, for 1 : 4 addition of hydrogen in the former case creates an asymmetric carbon atom at position 9, whereas no asymmetry is introduced in the latter case. The formation of a dibromide from *apo*cholic acid or of an 8 : 14-glycol from an 8 : 14-oxide leads directly to the two dienic acids by elimination of hydrogen bromide or of water from positions 14 : 15 on the one side and from either positions 8 : 9 or 8 : 7 on the other. It must be assumed that, when an oxide or bromide is not the intermediate compound, selenium dioxide attacks the tertiary carbon atom 9, whereas perbenzoic acid attacks the secondary carbon atom 7. The formation of the dienic acids from dihydroxycholenic acid or the oxide is explicable by attack on the tertiary carbon atom 8, but the decomposition of the oxide is not simple; however, since this decomposition is carried out in presence of acid, it is not unreasonable to assume that migration of the ethylenic linkages takes place.

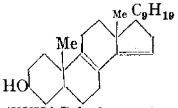
It is now possible to explain the reaction of selenium dioxide with dihydroergosterol described in Part I (*loc. cit.*). Ergosterol-*D* and ergosterol-B_3 are, respectively, the products from the immediate action of selenium dioxide and of the decomposition of the oxide. Ergosterol-*D*, $[\alpha]_D + 17°$ in chloroform, absorption maximum at 242 mμ, $E^{1\%}_{1\,\text{cm.}} = 540$, is considered to be the analogue of β-dihydroxycholadienic acid, $[\alpha]_D + 78°$ in alcohol, absorption maximum at 248 mμ, $E^{1\%}_{1\,\text{cm.}} = 430$; and ergosterol-$B_3$, $[\alpha]_D - 207°$ in chloroform, absorption maximum at 242 mμ, $E^{1\%}_{1\,\text{cm.}} = 255$, is the analogue of α-dihydroxycholadienic acid, $[\alpha]_D - 62°$ in alcohol (probably greater for the pure acid, see above), absorption maximum at 240—248 mμ, $E^{1\%}_{1\,\text{cm.}} = 240$. The reactions are, therefore, to be formulated :



(XIV.) Ergosterol-*D*. (XIII.) Dihydroergosterol. (XV.) Dihydroergosterol oxide.



(XVI.) Ergosterol-B_3.



(XVII.) Dehydroergostenol.

Preliminary experiments only have been carried out with α-ergostenol. Under the conditions employed, only one product was isolated, namely, dehydroergostenol, with the physical properties recorded in the literature, to which the formula (XVII) is now assigned. The possible formation of isomeric compounds should be worth investigation, particularly in view of the experiences of Windaus and Lüttringhaus (*Annalen*, 1930, **481**, 119) and of Laucht (*loc. cit.*), who obtained complex products by treatment of α-ergostenol with perbenzoic acid and with ozone, respectively.

Experimental.

apo*Cholic Acid and Selenium Dioxide*.—Solutions of *apo*cholic acid (20 g.) in absolute alcohol (250 c.c.) and selenium dioxide (16 g., 3 mols.) in water (150 c.c.) were mixed and kept at 37° for

16 hours. After cooling, the mixture of red selenium and white crystalline material was collected, washed with water, and stirred with sufficient sodium carbonate solution to dissolve the acid and after saturation with sodium sulphate and addition of a little charcoal the liquid was filtered and acidified with hydrochloric acid, yielding 12·1 g. of β-*dihydroxycholadienic acid*, m. p. 232—238°. This was recrystallised four times alternately from dilute acetic acid and glacial acetic acid, and finally crystallised by solution in hot alcohol containing a little ammonia and precipitation by the cautious addition of acetic acid. The m. p. was now constant at 253—255°; $[\alpha]_D^{20°}$ + 71·0°, $[\alpha]_{5461}^{20°}$ + 82·1° (*c*, 0·476); α_{5461}/α_D = 1·16. The absorption spectrum showed a maximum at 249 mμ ($E_{1\,cm.}^{1\%}$ = 430) with a subsidiary protuberance at about 242 mμ ($E_{1\,cm.}^{1\%}$ = 400) (Fig. 2).

The yield was lower (2 g. of crude product from 5 g.) when the reaction was carried out for 10 minutes on the water-bath; the product, recrystallised from methyl alcohol and dried over phosphoric oxide, had m. p. 251—252·5°; $[\alpha]_D^{20°}$ + 69°, $[\alpha]_{5461}^{20°}$ + 81·5° (*c*, 0·493); α_{5461}/α_D = 1·18 [Found (micro): C, 73·7; H, 9·2. $C_{24}H_{36}O_4$ requires C, 74·2; H, 9·3%].

Methyl apo*Cholate and Selenium Dioxide*.—Methyl *apo*cholate (Boedecker, *loc. cit.*), recrystallised from methyl alcohol, had m. p. 85—94° (Found: loss at 100°/0·1 mm., 7·4. $C_{25}H_{40}O_4$,MeOH requires loss 7·3%). The solvent-free substance had m. p. 112—115° [Found (micro): C, 73·7; H, 9·7. Calc. for $C_{25}H_{40}O_4$: C, 74·2; H, 10·0%]. A solution of the ester (1 g.) in alcohol (13·3 c.c.) was mixed with selenium dioxide (1 g.) in water (6·7 c.c.) and kept at 37° for 24 hours, the selenium (0·15 g.) removed, and the filtrate diluted with water. Ether extracted a gum, which was hydrolysed with alcoholic sodium hydroxide. The free acid, twice recrystallised from alcoholic ammonia by addition of acetic acid, had m. p. 254—257° and $[\alpha]_D^{20°}$ + 74° (*c*, 0·196). The absorption maximum was at 248 mμ ($E_{1\,cm.}^{1\%}$ = 480).

Methyl β-*dihydroxycholadienate* was prepared by refluxing the silver salt for 3 hours with methyl iodide. Extraction of the product with methyl alcohol and evaporation to dryness yielded a gum, which was crystallised from dilute acetic acid (1 : 1); after separation of a small amount of acid the ester crystallised; it was recrystallised and then had m. p. 87—89°; $[\alpha]_D^{20°}$ + 62·5°, $[\alpha]_{5461}^{20°}$ + 71° (*c*, 0·489); α_{5461}/α_D = 1·13. The absorption maximum was at 249 mμ ($E_{1\,cm.}^{1\%}$ = 377) [Found: (micro) C, 70·0; H, 9·1; (macro) loss at 95°/12 mm., 12·3. $C_{25}H_{38}O_4$,$C_2H_4O_2$ requires C, 70·1; H, 9·15; loss, 12·1%].

apo*Cholic Acid and Perbenzoic Acid*.—(*a*) The method of Wieland and Deulofeu (*loc. cit.*) was slightly modified. The solution resulting from the reaction of 10 g. of *apo*cholic acid was extracted with aqueous sodium hydroxide, the extract acidified with hydrochloric acid, and the oily precipitate washed with a little light petroleum and then with ether. Crystallisation from dilute acetic acid yielded 4 g. of crude acid, m. p. 228—237°. After three recrystallisations from dilute acetic acid and finally from alcoholic ammonia by addition of acetic acid, the dihydroxycholadienic acid had m. p. 252—255°, not depressed by the acid prepared with selenium dioxide, and $[\alpha]_D^{20°}$ − 35·3°, $[\alpha]_{5461}^{20°}$ − 47·7° (*c*, 0·457); α_{5461}/α_D = 1·35. The absorption spectrum showed a broad maximum at 243 mμ ($E_{1\,cm.}^{1\%}$ = 300).

The acid was converted through the silver salt into the methyl ester, an uncrystallisable gum being obtained. This was dried at 100°/10 mm. and treated with 3 : 5-dinitrobenzoyl chloride in pyridine; methyl α-bis-3′ : 5′-dinitrobenzoyloxycholadienate, isolated with some difficulty, was obtained in needles, m. p. 165—166·5°, after recrystallisation from ethyl acetate.

(*b*) By the method of Borsche and Todd (*loc. cit.*), interaction of *apo*cholic acid and perbenzoic acid in acetone and chloroform yielded *apo*cholic acid oxide, m. p. 201—205°, $[\alpha]_D^{20°}$ + 42°, $[\alpha]_{5461}^{20°}$ + 49° (*c*, 0·524); α_{5461}/α_D = 1·16; it showed no selective absorption in 0·5% alcoholic solution. The mother-liquor of the crude oxide yielded α-dihydroxycholadienic acid, m. p. 252—254°; $[\alpha]_D^{20°}$ − 62°, $[\alpha]_{5461}^{20°}$ − 81° (*c*, 0·229); α_{5461}/α_D = 1·33. The absorption spectrum showed a broad maximum at 240—248 mμ ($E_{1\,cm.}^{1\%}$ = 240) (Fig. 2).

Decomposition of apo*Cholic Acid Oxide*.—By the method of Borsche and Todd (*loc. cit.*), an acid was obtained, m. p. 248—251°; $[\alpha]_D^{20°}$ + 30°, $[\alpha]_{5461}^{20°}$ + 33° (*c*, 0·23); α_{5461}/α_D = 1·09. The absorption spectrum showed a fairly sharp maximum at 249 mμ ($E_{1\,cm.}^{1\%}$ = 420).

apo*Cholic Acid and Bromine*.—The method of Boedecker and Volk (*Ber.*, 1922, **55**, 2302) gave a 50% yield of a crude product, m. p. 230—236°, which, after crystallisation from dilute acetic acid, followed by alcoholic ammonia and acetic acid, had m. p. 248—251°, $[\alpha]_D^{28°}$ − 8·4°, $[\alpha]_{5461}^{28°}$ − 15·4° (*c*, 0·357); α_{5461}/α_D = 1·44. The absorption spectrum showed a broad maximum in the region of 245 mμ ($E_{1\,cm.}^{1\%}$ = 325).

Dihydroxycholadienic acid obtained from Dr. Boedecker.—This had m. p. 250—254°; $[\alpha]_D^{20°}$ + 18·9°, $[\alpha]_{5461}^{20°}$ + 19·5° (*c*, 0·424); α_{5461}/α_D = 1·03; broad absorption band with maximum at 248 mμ ($E_{1\,cm.}^{1\%}$ = 330).

Methyl Dihydroxycholenate.—The acid used was obtained from the J.D. Riedel-E. de Haen A.G., Berlin. It had m. p. 265—268°; $[\alpha]_{D}^{25°}$ + 64°, $[\alpha]_{D}^{25°}$ + 71° (*c*, 0·276); α_{5461}/α_D = 1·11. As its sparing solubility was an inconvenience, it was converted into the methyl ester by way of the silver salt. As a control of its purity, the ester was converted into the 3 : 5-dinitrobenzoate and recovered. After removal of solvent of crystallisation at 100°/10 mm., the ester was treated with 3 : 5-dinitrobenzoyl chloride in pyridine on the water-bath. *Methyl bis-3′ : 5′-dinitrobenzoyloxycholenate* formed pale yellow needles from ethyl acetate, m. p. 209—210·5° [Found (micro): C, 59·0; H, 5·8. $C_{39}H_{44}O_{14}N_4$ requires C, 59·1; H, 5·6%]. Hydrolysis with alcoholic sodium hydroxide and two recrystallisations from alcoholic ammonia and acetic acid (charcoal) yielded dihydroxycholenic acid, m. p. 269—271°; $[\alpha]_{D}^{25°}$ + 63°, $[\alpha]_{5461}^{25°}$ + 73° (*c*, 0·323); α_{5461}/α_D = 1·16. Reduction of the methyl ester in methyl alcohol with hydrogen and palladised charcoal, and hydrolysis, yielded deoxycholic acid, isolated as the acetic acid compound, m. p. 139—143°; $[\alpha]_{D}^{20°}$ + 48·3°, $[\alpha]_{5461}^{20°}$ + 58·0° (*c*, 0·404); α_{5461}/α_D = 1·20.

Methyl Dihydroxycholenate and Selenium Dioxide.—In the oxidation (ester 1 g., alcohol 13·3 c.c.; selenium dioxide 1 g., water 6·7 c.c.; kept at 37° for 24 hours) the precipitation of selenium began more slowly than with *apo*cholic acid. After removal of selenium (0·85 g.) the product was hydrolysed and worked up in the usual way. The recrystallised acid had m. p. 259—261°; $[\alpha]_{D}^{20°}$ + 21·7°, $[\alpha]_{5461}^{20°}$ + 21·1° (*c*, 0·196); α_{5461}/α_D = 0·975. The absorption spectrum showed a broad maximum at 242—249 mμ ($E_{1\,cm.}^{1\%}$ = 260). Another preparation (yield, 0·4 g. from 2 g.) had m. p. 259—262°; $[\alpha]_{D}^{27°}$ + 8·8°, $[\alpha]_{5461}^{27°}$ + 3·8° (*c*, 0·404); α_{5461}/α_D = 0·375. The absorption spectrum showed a broad maximum at 240—250 mμ ($E_{1\,cm.}^{1\%}$ = 343).

Methyl Dihydroxycholenate and Perbenzoic Acid.—The ester (2 g.) in chloroform (5 c.c.) was treated with 20 c.c. of a solution of perbenzoic acid in chloroform (0·006 g. of active oxygen *per* c.c.). The mixture became slightly warm. After 4 hours the solution was washed with aqueous sodium carbonate and evaporated to dryness, and the residue hydrolysed with alcoholic sodium hydroxide. After recrystallisation from alcoholic ammonia and acetic acid and again from dilute acetic acid, the product had m. p. 250—252°; $[\alpha]_{D}^{20°}$ + 16°, $[\alpha]_{5461}^{20°}$ + 12·5° (*c*, 0·30); α_{5461}/α_D = 0·78. The absorption spectrum showed a broad maximum at 245—250 mμ ($E_{1\,cm.}^{1\%}$ = 370).

Decomposition of Dihydroxycholenic Acid Oxide.—The oxide (Wieland and Deulofeu, *loc. cit.*), crystallised from ethyl acetate, had m. p. 180—181°; $[\alpha]_{D}^{20°}$ + 50°, $[\alpha]_{5461}^{20°}$ + 60° (*c*, 0·238); α_{5461}/α_D = 1·20. A 0·1% solution in alcohol showed no selective absorption, but when diluted to 0·002% with dilute sulphuric acid and kept for 24 hours it produced a band with a broad maximum at 240—250 mμ ($E_{1\,cm.}^{1\%}$ = 220). Decomposition of the oxide by warming in dilute aqueous-alcoholic sulphuric acid yielded a product, which, recrystallised from alcoholic ammonia and acetic acid, had m. p. 240—244°; $[\alpha]_{D}^{20°}$ + 34·5°, $[\alpha]_{5461}^{20°}$ + 41° (*c*, 0·315); α_{5461}/α_D = 1·18. The absorption spectrum showed a fairly sharp maximum at 249 mμ ($E_{1\,cm.}^{1\%}$ = 400).

Catalytic Reduction of β-Dihydroxycholadienic Acid.—The acid (3 g.) was reduced in glacial acetic acid solution (150 c.c.) with hydrogen and palladised charcoal (0·5 g. of palladous chloride on 5 g.); the volume of hydrogen absorbed in 2 hours was 180 c.c. (calc., 172·5 c.c.). The product was precipitated with water and recrystallised, first from alcohol (charcoal) containing xylene, and finally twice from acetic acid. The *acetic*-β-apo*cholic acid* obtained had m. p. 150—155°; $[\alpha]_{D}^{20°}$ + 73·5°, $[\alpha]_{5461}^{20°}$ + 86·5° (*c*, 0·435); α_{5461}/α_D = 1·18. The absorption spectrum showed slight absorption at 240—250 mμ corresponding to the presence of about 0·3% of unreduced β-dihydroxycholadienic acid ($E_{1\,cm.}^{1\%}$ = 1·3) [Found (micro): C, 69·9; H, 9·5. $C_{24}H_{38}O_4,C_2H_4O_2$ requires C, 69·3; H, 9·4%]. Freed from acetic acid by recrystallisation from aqueous alcohol, and dried at 120° in a vacuum, the free β-apo*cholic acid* had m. p. 163—165°; $[\alpha]_{D}^{20°}$ + 78·5°, $[\alpha]_{5461}^{20°}$ + 92·4° (*c*, 0·361); α_{5461}/α_D = 1·18. Another specimen of the acetic acid compound, prepared in the same way, had $[\alpha]_{D}^{20°}$ + 74·8°, $[\alpha]_{5461}^{20°}$ + 88·4° (*c*, 0·477); α_{5461}/α_D = 1·18; the absorption corresponded to 0·5% of unreduced acid. *Xylene*-β-apo*cholic acid*, prepared by crystallisation from alcohol containing a little xylene, and dried in a vacuum over phosphoric oxide, had m. p. 156·5—161°; $[\alpha]_{D}^{20°}$ + 69·7°, $[\alpha]_{5461}^{20°}$ + 82·5° (*c*, 0·665); α_{5461}/α_D = 1·18 [Found (micro): C, 75·7; H, 9·9. $C_{24}H_{38}O_4,0·5C_8H_{10}$ requires C, 75·8; H, 9·8%]. *Methyl* β-apo*cholate*, prepared from the silver salt and methyl iodide and recrystallised from aqueous methyl alcohol, had m. p. 84—87°; $[\alpha]_{D}^{20°}$ + 79°, $[\alpha]_{5461}^{20°}$ + 90° (*c*, 0·246); α_{5461}/α_D = 1·14 [Found, in air-dried material: (micro) C, 70·0; H, 10·2; loss at 80°/0·1 mm. over phosphoric oxide (macro), 6·2. Found for solvent-free material (micro): C, 73·7; H, 10·0. $C_{25}H_{40}O_4,1·5H_2O$ requires C, 69·6; H, 10·0; loss, 6·3%. $C_{25}H_{40}O_4$ requires C, 74·2; H, 10·0%].

β-apo*Cholic Acid and Selenium Dioxide.*—Acetic-β-*apo*cholic acid (0·5 g.) was treated with selenium dioxide in the usual way. The product was not exhaustively purified, owing to its

small amount. Recrystallised from dilute acetic acid, it had m. p. 233—240°; $[\alpha]_D^{20°} + 77.7°$, $[\alpha]_{5461}^{20°} + 92.8°$ (*c*, 0·285); $\alpha_{5461}/\alpha_D = 1.20$. The absorption spectrum showed a maximum at 250 mμ ($E_{1\,cm.}^{1\%} = 310$).

β-*apo*Cholic *Acid and Perbenzoic Acid*.—The recrystallised product had m. p. 246—250°; $[\alpha]_D^{20°} + 36.5°$, $[\alpha]_{5461}^{20°} + 41.5°$ (*c*, 0·278); $\alpha_{5461}/\alpha_D = 1.14$; absorption maximum at 248 mμ ($E_{1\,cm.}^{1\%} = 395$).

Catalytic Reduction of α-Dihydroxycholadienic Acid.—The acid (2 g.) in acetic acid (100 c.c.), with palladised charcoal (0·5 g. of palladous chloride on 5 g.), absorbed 125 c.c. of hydrogen in 1½ hours (calc., 115 c.c.). The acetic-*apo*cholic acid, precipitated by water and recrystallised from acetic acid, had m. p. 140—155°; $[\alpha]_D^{20°} + 42.3°$, $[\alpha]_{5461}^{20°} + 50.4°$ (*c*, 0·479); $\alpha_{5461}/\alpha_D = 1.19$ [Found (micro): C, 69·1; H, 9·2. Calc. for $C_{24}H_{38}O_4,C_2H_4O_2$: C, 69·3; H, 9·4%]. It was converted into the xylene compound, m. p. 165—169°; $[\alpha]_D^{20°} + 39.6°$, $[\alpha]_{5461}^{20°} + 46.3°$ (*c*, 0·6295); $\alpha_{5461}/\alpha_D = 1.17$ [Found (micro): C, 75·3; H, 9·8. Calc. for $C_{24}H_{38}O_4,0.5C_8H_{10}$: C, 75·8; H, 9·8%].

α-Ergostenol and Selenium Dioxide.—α-Ergostenol (1 g.), m. p. 130—133°, and selenium dioxide (1 g.) in 75% aqueous alcohol (200 c.c.) were kept for 16 hours; little reaction occurred. The mixture was refluxed for 1 hour, and the selenium (0·1 g.) removed by filtration. The product (0·8 g.) separated on cooling; m. p. 123—127°. It was acetylated by boiling with acetic anhydride for 15 minutes. After three recrystallisations from alcohol and finally from ethyl acetate, dehydroergostenyl acetate was obtained, m. p. 136—137°; $[\alpha]_D^{20°} - 34.3°$, $[\alpha]_{5461}^{20°} - 43.6°$ in chloroform (*c*, 0·45); $\alpha_{5461}/\alpha_D = 1.28$. Hydrolysis and recrystallisation from alcohol yielded dehydroergostenol, m. p. 139·5—141°; $[\alpha]_D^{20°} - 17.5°$, $[\alpha]_{5461}^{20°} - 23°$ in chloroform (*c*, 0·2575); $\alpha_{5461}/\alpha_D = 1.32$. Another preparation was converted into the 3 : 5-*dinitrobenzoate*, which formed yellow prisms from ethyl acetate, m. p. 163—166°; $[\alpha]_D^{20°} - 3.0°$, $[\alpha]_{5461}^{20°} - 5.7°$ in benzene (*c*, 0·437) [Found (micro): C, 70·8; H, 8·2. $C_{35}H_{48}O_6N_2$ requires C, 70·9; H, 8·2%].

Note on Physical Measurements.—The m. p.'s were all observed in an electrically heated block with short-stem thermometers, and are, therefore, "corrected." The optical rotations were measured in a 4 dm. tube; all solutions were in absolute alcohol unless otherwise stated. I am indebted to Dr. F. A. Askew, formerly of this Institute, and to E. H. Pitte, our technical assistant, for most of the absorption measurements, which were made in 0·002% or 0·003% alcoholic solution by the method described by Philpot and Schuster (*Medical Research Council, Special Report Series*, 1933, No. 177).

SUMMARY.

The action of selenium dioxide on *apo*cholic acid yields the dextrorotatory β-dihydroxycholadienic acid, and the action of perbenzoic acid yields the lævorotatory α-dihydroxycholadienic acid. The "dihydroxycholadienic acids" described in the literature, formed by other methods, are mixtures of these two isomerides, as are also the products obtained from dihydroxycholenic acid. The α- and the β-dienic acid have identical m. p.'s, but different absorptions in the ultra-violet region. The α-acid is catalytically reduced to *apo*cholic acid, and the β-acid yields β-*apo*cholic acid, distinguished by its higher dextrorotation. It is concluded that *apo*cholic acid and dihydroxycholenic acids are $\Delta^{8:14}$- and $\Delta^{14:15}$-compounds, respectively, and that α- and β-dihydroxycholadienic acid are $\Delta^{7:8-14:15}$- and $\Delta^{9:8-14:15}$-compounds, respectively. The two *apo*cholic acids differ in the configuration of carbon atom 9.

Further consideration of the results described in Part I (Callow and Rosenheim, J., 1933, 387) indicates that ergosterol-*D*, formed by the interaction of dihydroergosterol and selenium dioxide, is the $\Delta^{9:8-14:15-22:23}$-compound, and the oxide formed at the same time is the $\Delta^{8:14}$-compound and yields the $\Delta^{7:8-14:15-22:23}$-compound, ergosterol-B_3, on decomposition.

I am indebted to Dr. O. Rosenheim for much helpful criticism and discussion of these results.

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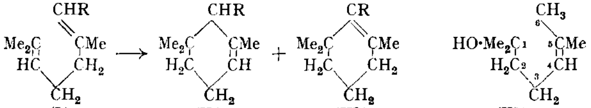
112. *Fused Carbon Rings. Part VII. The Preparation of Cyclic Hydrocarbons from Unsaturated Tertiary Alcohols. The Synthesis of* cis-*9-Methyl-octalin and -decalin, and a Proof of the Presence of the Angular Methyl Group.*

By D. C. Hibbit and R. P. Linstead.

The main object of this work was to devise a method for the synthesis of polycyclic compounds containing an angular methyl group. This was intended to serve as a model for subsequent attempts at the preparation of substances of the type of sterols, sex-hormones, and the eudesmol group of sesquiterpenes. Much of the evidence for the existence of the angular group in these natural products is indirect, depending on the fact that it is eliminated during dehydrogenation. With a view to increasing the control over this method it was hoped during this work to prove the presence of the angular methyl group in suitable compounds *by methods independent of their synthesis* and then to examine their behaviour on dehydrogenation.

The synthetic method which we have studied is connected with the work of Tiemann and Semmler on the cyclisation of geraniolene and its derivatives. These chemists showed that dienes of type (I) are cyclised in good yield to the isomeric monocyclic compounds (II) and (III), containing one double bond, by treatment with sulphuric acid (see particularly *Ber.*, 1893, **26**, 2717; 1900, **33**, 3711).

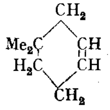


(I.) (II.) (III.) (IV.)

This reaction appears to be independent of the nature of the group R, and has been observed *inter alia* when R is H (geraniolene), Me (dihydromyrcene), CH_2·OAc (geranyl acetate), and CO_2H (geranic acid). The proportions of the forms (II) and (III) in the products vary with the nature of R and the conditions of cyclisation, but the α-form (II) generally predominates. Allied to these cyclisations is one by which Harries and Weil (*Ber.*, 1904, **37**, 848) prepared α-*cyclo*geraniolene (II, R = H) in good yield by the action of phosphoric acid on the dimethylheptenol (IV).

It appeared that such a *cyclo*-dehydration might have general synthetic possibilities and we accordingly examined a number of alcohols of allied structure with a view to finding what features were necessary for the reaction. The *gem*-dimethyl group at C_1 was retained for obvious reasons, the methyl group at C_5 was removed, and the length of the chain and the position of the double bonds were varied. The required unsaturated alcohols (V—VIII) were prepared by the action of methylmagnesium iodide on the esters of the appropriate pentenoic or hexenoic acids. All of these were available in a state of purity and the positions of the double bond were known with certainty (Linstead and Rydon, J., 1934, 1998; Letch and Linstead, *ibid.*, p. 1994; Boxer and Linstead, J., 1931, 740).

(V.) $CMe_2(OH)·CH_2·CH_2·CH{:}CH_2$
(VI.) $CMe_2(OH)·CH_2·CH{:}CH·CH_2Me$
(VII.) $CMe_2(OH)·CH_2·CH_2·CH{:}CHMe$
(VIII.) $CMe_2(OH)·CH_2·CH_2·CH_2·CH{:}CH_2$ ⟶
(X.) $CMe_2(OH)·CH_2·CH_2·CH_2·CHMe·OH$



(IX.)

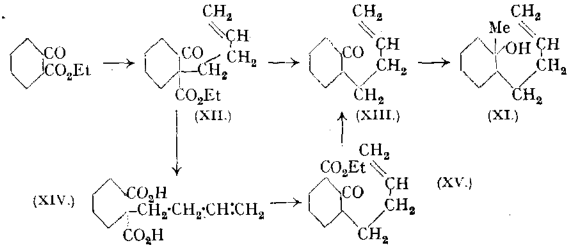
Treatment of the alcohols (V), (VI), and (VII) with phosphoric acid yielded the corresponding open-chain dienes or their polymerides, and no cyclisation could be detected. Dimethyl-Δ^3-butenylcarbinol (V) also gave no cyclic hydrocarbon on treatment with sulphuric acid.

Dimethyl-Δ^4-pentenylcarbinol (VIII), on the other hand, gave 1 : 1-dimethyl-Δ^3-*cyclo*hexene (IX) in good yield when treated with phosphoric acid.

The negative results obtained with (V), (VI), and (VII) show that there is no tendency to form a *cyclo*pentene ring under these conditions (contrast the work of Bogert and Davidson in the aromatic series; see p. 477). It is interesting that (VII) fails to yield a *cyclo*hexene, whereas its 5-methyl derivative (IV) does so readily. A reasonable explanation is that the 5-methyl group exercises its usual ability to promote the addition of acid to the double bond. The additive compound so formed then decomposes to give the olefinic alcohol with the terminal double bond (corresponding to VIII), which subsequently cyclises. It appears improbable that dihydric alcohols (such as X) intervene in these cyclisations (IV ⟶ II, VIII ⟶ IX), as, if this were true, it would be expected that the cyclisation of (VII) would be possible. The possible intervention of dienes is discussed in the next paper.

The structure of (IX) follows from its physical properties, from its reactions with one molecular proportion of bromine and of hydrogen, and from its oxidation to ββ-dimethyladipic acid. This fixes the position of the double bond, which corresponds to that of α-*cyclo*geraniolene. Catalytic hydrogenation yielded 1 : 1-dimethyl*cyclo*hexane. The physical constants of both (IX) and its reduction product agreed substantially with those recorded in the literature.

From these results it was anticipated that 1-*methyl*-2-$\Delta^{3'}$-*butenyl*cyclo*hexanol* (XI) would cyclise readily to a 9-methyloctalin. This alcohol was synthesised by the method given below, which establishes the structure :



Condensation of Δ^3-butenyl bromide and ethyl sodio*cyclo*hexanone-2-carboxylate in toluene yielded 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone*-2-*carboxylate* (XII), which when hydrolysed by baryta gave mainly 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone* (XIII). It is common for hydrolyses of this type to yield principally the corresponding pimelic acid (cf. Kon, J., 1933, 1081); but ring fission was subsidiary in the present instance. The crude acid which it yielded was purified through the ester, and the *ethyl* 1-$\Delta^{3'}$-*butenylpimelate* converted by the Dieckmann process into *ethyl* 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone*-6-*carboxylate* (XV). On hydrolysis, this yielded 2-butenyl*cyclo*hexanone, identical with that prepared by the direct hydrolysis of (XII), together with a little 1-$\Delta^{3'}$-*butenylpimelic acid* (XIV). 2-$\Delta^{3'}$-Butenyl*cyclo*hexanone smoothly yielded 1-*methyl*-2-$\Delta^{3'}$-*butenyl*cyclo*hexanol* with methylmagnesium iodide.

Preliminary experiments on the preparation of this alcohol from butenylmagnesium bromide and 1-methyl*cyclo*hexene oxide or 2-chloro-1-methyl*cyclo*hexanol yielded rather poor yields of material of doubtful homogeneity and the method was not pursued. It is possible that some rearrangement of the carbon skeleton occurred (cf. Cook, Hewett, and Lawrence, this vol., p. 71).

1-Methyl-2-$\Delta^{3'}$-butenyl*cyclo*hexanol gave a methyloctalin in good yield when dehydrated with phosphoric acid. The reaction required a rather higher temperature than that used in the preparation of dimethyl*cyclo*hexene (130° against 95°). From the evidence given below, the product is mainly cis-9-*methyl*-Δ^2-*octalin* (XVI). The position of the double

bond is taken by analogy with dimethyl*cyclo*hexene and *cyclo*geraniolene. Oxidation yielded derivatives corresponding to the 9-position of the methyl group. Owing to the occurrence of more fundamental oxidation these were isolated in only 36% yield: hence we cannot exclude the possibility that some 8-methyloctalin, formed by an indirect process of dehydration and cyclisation, was present. For the sake of simplicity we shall for the present assume that the hydrocarbon is entirely the 9-methyl derivative. The dehydrogenation of the hydrocarbon and its reduction product is being studied.

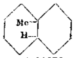
From its physical properties the hydrocarbon contained two rings and one double bond. It reacted with one molecular proportion of hydrogen over platinum. The properties of the 9-*methyldecalin* so obtained showed that it belonged to the *cis*-series (XVII). It differed from the synthetic *trans*-9-methyldecalin of Ruzicka, Koolhaas, and Wind (*Helv. Chim. Acta*, 1931, **14**, 1151) in the same way as *cis*-decalin differs from its *trans*-isomeride:

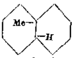
Substance.	B. p.	$d_{4^\circ}^{t^\circ}$.	$n_{4^\circ}^{t^\circ}$.	*t*.	$[R_L]_D$.	EM_D.
cis-Decalin (H.)	72°/12 mm.	0·898	1·4823	20°	43·88	−0·10 }
trans-Decalin (H.)	63/12 ,,	0·872	1·4713	20	44·26	+0·28 }
cis-9-Methyldecalin (H.L.)	82/11 ,,	0·8909	1·4813	16·1	48·63	+0·03 }
trans-9-Methyldecalin (R.K.W.)	70/12 ,,	0·8583	1·4631	20	48·82	+0·22 }
,, (H.L.)	70/11 ,,	0·8654	1·4697	17·6	49·03	+0·43 }

(H., Hückel; R.K.W., Ruzicka, Koolhaas, and Wind; H.L., present work.) These figures should be compared with the table given by Ruzicka, Koolhaas, and Wind (*loc. cit.*, p. 1174).

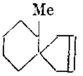
It has been shown by Zelinski and Turova-Pollak (*Ber.*, 1929, **62**, 1658; 1932, **65**, 1299) that *cis*-decalin is converted into the *trans*-isomeride by aluminium chloride at room temperature. We now find that the same reaction occurs with *cis*-9-methyldecalin; the product (XVIII) after careful purification had the properties shown in the last line of the table. The fall in the physical constants and the rise in molecular refractivity clearly show the change to the *trans*-series; the difference between our values for the molecular refractivity of *cis*- and *trans*-9-methyldecalin is 0·40, almost identical with that found by Hückel for the parent compounds. This change supports the *cis*-configuration for the primary product (XVI).

(XVI.)

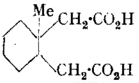

(XVII.)


(XVIII.)

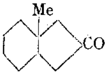
On oxidation with alkaline permanganate the hydrocarbon (XVI, $C_{11}H_{18}$) yielded a saturated monocyclic dibasic acid, $C_{11}H_{18}O_4$. This substance, m. p. 160—163°, contained a small amount of a persistent isomeric impurity which was isolated by fractional ketonisation (Barrett and Linstead, J., 1935, 436). When the crude acid was heated to 280° with a trace of baryta, it gave a good yield of a mixture of two saturated dicyclic ketones, $C_{10}H_{16}O$, the semicarbazones of which melted at 220° and 238°. The ketone giving the higher-melting semicarbazone was present only in small amount. The formation of ketone shows that the acids must be substituted adipic acids derived from a *cyclo*hexene ring and the original hydrocarbon must therefore be a methyloctalin and not a spiran such as (XIX). The remote possibility that the hydrocarbon contains a 7-membered ring is excluded by the results of oxidation of the ketone.



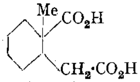
(XIX.)



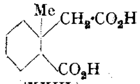
(XX.)



(XXI.)



(XXII.)



(XXIII.)

From the residue of the ketonisation a small amount of a pure acid, $C_{11}H_{18}O_4$, m. p. 195°, was recovered. When this was heated with baryta under rather more vigorous conditions, it gave the ketone forming the semicarbazone, m. p. 238°. We consider the acid of m. p. 160—163° to be nearly pure cis-1-*methyl*cyclo*hexane*-1 : 2-*diacetic* acid (XX) and that of m. p. 195° to be the trans-*isomeride*, which is cyclised a little less readily. The ketones with

semicarbazones, m. p. 220° and 238°, are respectively the *cis*- and the *trans*-form of *8-methyl-2-hydrindanone* (XXI). [The diacetic acid formula, corresponding to the Δ^2-position of the double bond, is not finally established. The alternative, which is much less probable, is that one or both of the acids $C_{11}H_{18}O_4$ is a 1-methyl*cyclo*hexane-1-carboxylic-2-propionic acid, in which case the corresponding ketone would be an 8-methyl-1-hydrindanone.]

The mixture of ketones (mainly *cis*-) on oxidation with nitric acid gave a mixture of dibasic acids, $C_{10}H_{16}O_4$, m. p.'s 175° and 162—164°, the latter present in small amount. The structures of both these acids have been proved by their synthesis (see Part IX, this vol., p. 480, where the evidence for their configuration is discussed). The acid of m. p. 175° is cis-1-*methyl*cyclo*hexane-1-carboxylic-2-acetic acid* (XXII); the other is the *trans*-isomeride. Owing to the presence of the methyl group attached to the carbon atom carrying the carboxyl group, which prevents enolisation, these acids cannot be interconverted. The identity of the acids obtained by degradation and by synthesis proves conclusively the presence of the angular methyl group in the ketone and the parent methyloctalin. The ketone (XXI) is not oxidised to the isomeric acid (XXIII), both forms of which have been synthesised. The relationship of our acids with those recently described by Clemo and Chuang and their collaborators is discussed in Part IX (*loc. cit.*).

A preliminary account of this work appeared in March, 1935 (*Chem. and Ind.*, 1935, **54**, 315). Cohen, Cook, and Hewett have described some related experiments on 2-methyl-1-$\Delta^{3'}$-butenyl-3 : 4-dihydrophenanthrene (J., 1935, 1633; cf. Cook, *Chem. and Ind.*, *loc. cit.*). This was not cyclised by formic acid, but—from the evidence of dehydrogenation—yielded a tetracyclic substance with sulphuric acid in acetic acid. We had independently studied the simplest cyclisation of this type, namely, that of 2-methyl-1-butenyl*cyclo*hexanol (see following paper).

Experimental.

(1) *Preparation of Acyclic Alcohols.*—(*a*) Allylacetic acid, m. p. − 23° (Linstead and Rydon, *loc. cit.*), was converted into dimethyl-Δ^3-butenylcarbinol (V) by the method of Perkin and Pickles (J., 1905, **87**, 657). Yield 82%, b. p. 142—143°, m. p. − 22° to − 23° (corr.).

(*b*) The preparation of Δ^3-butenol from allyl bromide (Linstead and Rydon, J., 1934, 1998) gave an average yield of 42% of material of b. p. 112—116° on a 3 g.-molecular scale. The alcohol was converted through Δ^3-butenylmalonic acid, m. p. 92°, into Δ^5-*n*-hexenoic acid and its ethyl ester, b. p. 68—70°/23 mm., by the methods described in the last reference. 90 G. of ethyl Δ^5-*n*-hexenoate were added in portions to the Grignard reagent prepared from 385 g. of methyl iodide and 62 g. of magnesium in 1200 c.c. of dry ether; a gentle reaction ensued. After 12 hours, the product was decomposed with ice and dilute sulphuric acid, the ethereal layer washed with sodium sulphite solution, the ether removed, and the residue freed from unchanged ester by boiling with a little methyl-alcoholic potash for 4 hours. The neutral material, isolated in the usual way, yielded 77 g. (89%) of *dimethyl-Δ^4-pentenylcarbinol* (VIII) as a strong-smelling oil, b. p. 65—66°/15 mm., liquid at − 74°, $n_D^{18.7°}$ 1·4393, $d_{4°}^{18.7°}$ 0·8393, $[R_L]_D$ 40·18 (calc. 40·20) (Found: C, 74·7; H, 12·5. $C_8H_{16}O$ requires C, 74·9; H, 12·6%). 1 G. was left for 16 hours in a sealed tube with 0·93 g. of phenyl *iso*cyanate. The *phenylurethane* so obtained formed delicate needles from methyl alcohol, m. p. 67—68° (Found: C, 72·4; H, 8·5. $C_{15}H_{21}O_2N$ requires C, 72·8; H, 8·6%). The 3 : 5-dinitrobenzoate could not be obtained solid.

(*c*) Ethyl Δ^4-*n*-hexenoate, b. p. 68°/19 mm., was prepared from dihydrosorbic acid by the method of Letch and Linstead (*loc. cit.*; yield, 20 g. from 74 g.). From it *dimethyl-Δ^3-pentenylcarbinol* (VII) was prepared by the method described above for the Δ^4-isomeride. Yield 91%, b. p. 70°/17 mm., $n_D^{15.2°}$ 1·4429, $d_{4°}^{15.2°}$ 0·8397, $[R_L]_D$ 40·45 (calc., 40·20) (Found: C, 74·9; H, 12·6%). The *phenylurethane* melted at 89° (Found: C, 73·3; H, 8·3%). On oxidation of the carbinol with ice-cold alkaline permanganate, acetone (2 : 4-dinitrophenylhydrazone, m. p. 125—128°) and acetic acid (*p*-bromophenacyl ester, m. p. 87°) were formed. This confirms the penultimate position of the double bond.

(*d*) Ethyl Δ^2-*n*-hexenoate, b. p. 74°/27 mm., prepared from butaldehyde by the method of Boxer and Linstead (*loc. cit.*), was converted into *dimethyl-Δ^2-pentenylcarbinol* (VI) in the same way. Yield 83%, b. p. 63—64°/20 mm., m. p. − 27° to − 28° (corr.), $n_D^{14.4°}$ 1·4407, $d_{4°}^{14.4°}$ 0·8424, $[R_L]_D$ 40·15 (calc., 40·20) (Found: C, 74·7; H, 12·55%).

(2) *Dehydrations.*—(*a*) On dehydration with potassium hydrogen sulphate, dimethyl-Δ^3-

butenylcarbinol yielded allyl*iso*propenylmethane, b. p. 90—93°; nitrosochloride, m. p. 75° (cf. Perkin and Pickles, *loc. cit.*). When the carbinol (8 g.) was shaken with 36 c.c. of syrupy phosphoric acid (*d* 1·75), no heat was developed. The mixture was heated under reflux at 160° for ½ hour, and the upper layer then distilled off in a stream of carbon dioxide. The hydrocarbon in the distillate was extracted with a little ether, washed with sodium carbonate solution, and dried over calcium chloride. Distillation gave 2·5 g. of a product boiling indefinitely between 60° and 200°, which smelt of diene but was mainly polymeric. A similar product was obtained when the carbinol was shaken with 5 vols. of ice-cold sulphuric acid (60% by vol.). No fraction corresponding to a dimethyl*cyclo*pentene could be isolated in either case.

(*b*) 5 G. of dimethyl-Δ^4-pentenylcarbinol were shaken with 24 c.c. of syrupy phosphoric acid. The temperature rose to 50°; dehydration was completed by heating the mixture on the steam-bath for an hour. The acid layer assumed a reddish-brown colour, which subsequently spread to the upper layer and deepened. The product was isolated as before, 3·5 g. (81%) of 1 : 1-dimethyl-Δ^3-*cyclo*hexene, b. p. 128—129°/780 mm., being obtained. This was not quite pure after one redistillation over sodium (Found : C, 86·6; H, 12·8. Calc. for C_8H_{14} : C, 87·2; H, 12·8%). A preparation from 23 g. of the carbinol in which the mixture was heated at 160° for 1 hour gave 67% of product, b.p. 120—130°, which after two fractionations over sodium yielded the pure hydrocarbon; this had a powerful, rather pleasant, odour, b. p. 120—122°/760 mm., $n_D^{16·6°}$ 1·4479, $d_{4°}^{16·6°}$ 0·8092, $[R_L]_D$ 36·47 (calc. 1|= 36·48) (Found : C, 87·3; H, 12·6%). von Auwers and Lange (*Annalen*, 1915, **409**, 166) found b. p. 121°/750 mm., $n_D^{20°}$ 1·4456, $d_{4°}^{20°}$ 0·804. If the phosphoric acid was freshly dehydrated at 220° before use, only a poor yield of cyclic hydrocarbon was obtained together with a considerable quantity of polymeride. By the method of Rosenmund and Kuhnhenn (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154) the pure hydrocarbon added 159·8, 159·3 g. of bromine per mol. (calc. for one double bond, 159·8).

5·7 G. of 1 : 1-dimethyl-Δ^3-*cyclo*hexene were shaken with 1650 c.c. of aqueous ice-cold 2% potassium permanganate containing 5·5 g. of sodium carbonate. After 6 hours the unchanged hydrocarbon was removed in steam, the solution filtered, and the filtrate and washings evaporated to small bulk. The residue was acidified and extracted continuously with ether for 24 hours. The residue obtained by removal of the ether from the extract was purified through sodium bicarbonate in the usual manner and yielded a viscous oil, which crystallised in needles (2·8 g.) on standing in a vacuum; m. p. after crystallisation from water, and mixed m. p. with authentic ββ-dimethyladipic acid, 88° (Found : C, 55·35; H, 8·2. Calc. for $C_8H_{14}O_4$: C, 55·2; H, 8·1%).

1·34 G. of 1 : 1-dimethyl-Δ^3-*cyclo*hexene were hydrogenated without a solvent, Adams's catalyst being used; 267 c.c. of hydrogen, corresponding to 98% hydrogenation, were absorbed. After distillation over sodium, 0·95 g. of 1 : 1-dimethyl*cyclo*hexane, b. p. 120°, were obtained, $n_D^{17·6°}$ 1·4351, $d_{4°}^{17·6°}$ 0·7890, $[R_L]_D$ 37·08 (calc., 36·9) (Found : C, 84·9; H, 14·1. Calc. for C_8H_{16} : C, 85·6; H, 14·4%). The physical constants are very slightly higher than those in the literature (*e.g.*, v. Auwers and Lange, *loc. cit.*), possibly owing to the presence of a trace of unsaturated hydrocarbon.

(*c*) Dimethyl-Δ^3-pentenylcarbinol on treatment with phosphoric acid gave a hydrocarbon, b. p. 76—180°, smelling of diene, from which no definite substance could be isolated. Dimethyl-Δ^2-pentenylcarbinol gave the corresponding diene, partly polymerised, on treatment both with anhydrous potassium sulphate and with phosphoric acid. This was not further investigated.

(3) 9-*Methyloctalin.*—*cyclo*Hexanone-2-carboxylic ester (240 g., 15% excess) was added to 27·2 g. (1 mol.) of " molecular " sodium in 1400 c.c. of sodium-dry toluene, and the formation of sodio-compound completed by an hour's heating at 130°. The cooled product was treated with 160 g. (1 mol.) of Δ^3-butenyl bromide, and the mixture heated under reflux at 130° for 63 hours. The product was decomposed with ice and acid and extracted with ether, the extract washed with sodium bicarbonate solution and water, dried, and evaporated; fractionation of the residue gave a 70% yield of *ethyl* 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone-2-carboxylate* (XII), b. p. 134—143°/11 mm., and 156—158°/25 mm. on refractionation (Found : C, 69·2; H, 9·0. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%). No condensation product was obtained in boiling light petroleum (b. p. 60—80°), and the yield was only 30% in toluene at 130° after 20 hours. 13 G. of ethyl butenyl*cyclo*hexanonecarboxylate were refluxed with a solution of 26 g. of baryta in 4 vols. of water for 14 hours. The cold product was acidified and extracted with ether, and the extract washed thoroughly with sodium bicarbonate solution. The neutral product gave 4·6 g. (63%) of 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone* (XIII), b. p. 110—112°/23 mm. This yielded 6 g. of a *semicarbazone*, m. p. 125°, which crystallised from dilute alcohol in lustrous plates, m. p. 127° (Found : C, 63·1; H, 9·1. C[illegible]H[illegible]ON[illegible] requires C, 63·2; H, 9·2%). From this the ketone was regener-

ated by Kon's method (J., 1930, 1616) in 67% yield; b. p. 112—114°/28 mm. (Found: C, 78·8; H, 10·4. $C_{10}H_{16}O$ requires C, 78·95; H, 10·5%). On a larger scale 183 g. of the keto-ester yielded 78 g. of crude or 67 g. (45%) of pure ketone (b. p. 97—100°/15 mm.), together with 78 g. of acidic material. Acid hydrolysis of 2-butenyl*cyclo*hexanonecarboxylic ester was unsatisfactory.

Direct ketonisation of the acidic by-product with baryta was unsatisfactory. 40 G. were esterified in the cold with alcoholic sulphuric acid and the product, isolated in the usual way, was fractionated into ethyl pimelate, b. p. 136°/9 mm., and 26 g. of *ethyl* 1-$\Delta^{3'}$-*butenylpimelate*, b. p. 156—160°/9 mm. Refractionation gave 21 g., b. p. 161—162°/11 mm. (Found: C, 66·35; H, 9·6. $C_{15}H_{26}O_4$ requires C, 66·7; H, 9·6%). The ester was refluxed for 18 hours with 1·95 g. of sodium in 100 c.c. of light petroleum (b. p. 40—60°), and the product worked up. After two fractionations, 10 g. of *ethyl* 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone*-6-*carboxylate* (XV), b. p. 146—148°/11 mm., were isolated (Found: C, 69·2; H, 9·0. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%). Hydrolysis of this with baryta gave a 67% yield of 2-$\Delta^{3'}$-butenyl*cyclo*hexanone, b. p. 95—97°/11 mm., identical with that already prepared (semicarbazone, m.p. and mixed m. p. 126°). The bicarbonate washings of the last hydrolysis gave on acidification and ether extraction an oily acid which slowly crystallised. 1-$\Delta^{3'}$-*Butenylpimelic acid* (XIV) crystallised from ether in slender needles, or very slowly from water in transparent cubes, m. p. 39° [Found: C, 61·9; H, 8·3; equiv., 108. $C_{11}H_{18}O_4$ requires C, 61·6; H, 8·5%; equiv. (dibasic), 107].

41 G. of 2-$\Delta^{3'}$-butenyl*cyclo*hexanone were added in drops to a solution of methylmagnesium iodide prepared from 7·1 g. of magnesium in 450 c.c. of dry ether; the reaction was fairly vigorous; after 12 hours, the product was decomposed with ice and a slight excess of acetic acid, and 1-*methyl*-2-$\Delta^{3'}$-*butenyl*cyclo*hexanol* (XI) isolated by means of ether in 91% yield, b. p. 97—102°/11 mm. Refractionation gave 39 g., b. p. 102—104°/13 mm., $n_D^{17\cdot 6°}$ 1·4814, $d_{4°}^{17\cdot 6°}$ 0·9252, $[R_L]_D$ 51·77 (calc., 51·86), which did not solidify at − 70° (Found: C, 78·4; H, 11·7. $C_{11}H_{20}O$ requires C, 78·5; H, 11·9%). It was essential to remove all traces of iodine from this alcohol before distillation, otherwise catalytic decomposition to the diene occurred.

When 15 g. of the alcohol were mixed with syrupy phosphoric acid (*d* 1·75; 4 vols.), the temperature rose to 40°. The mixture was heated for 30 minutes at 140°, cooled, diluted with an equal volume of water, and extracted with purified light petroleum (b. p. 40—60°). The extract was washed with aqueous soda and water and dried with calcium chloride. Fractional distillation over sodium yielded 12 g. (89%) of cis-9-*methyl*-Δ^2-*octalin* (XVI), b. p. 82°/14 mm., $n_D^{15\cdot 2°}$ 1·4943, $d_{4°}^{15\cdot 2°}$ 0·9085, $[R_L]_D$ 48·13 (calc. for 1 $|\!\overline{=}$, 48·13) (Found: C, 87·9; H, 12·0. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%). When the dehydration was carried out at 95° for 30 minutes, the yield was 54%. Reaction with bromine under Rosenmund and Kuhnhenn's conditions apparently led to bromination, for the results were high for one double bond (Found: bromine addition per g.-mol., 205; calc., 159·8).

6·3 G. of 9-methyloctalin were catalytically reduced over Adams's platinum oxide; the volume of hydrogen absorbed corresponded to that calculated for $C_{11}H_{18}$ with one double bond. The reduced hydrocarbon was shaken successively with warm 2% potassium permanganate solution and concentrated sulphuric acid to remove any trace of octalin and was distilled over sodium; 5 g. of cis-9-*methyldecalin* (XVII) were obtained with the physical properties given on p. 472 (Found: C, 86·5; H, 13·1. $C_{11}H_{20}$ requires C, 86·75; H, 13·25%). 2·6 G. of this material were kept for several days in contact with 1·04 g. ($\frac{1}{2}$ mol.) of aluminium chloride with exclusion of water. There was no apparent reaction. The product was washed with water, dried, and distilled. Yield of *trans*-9-methyldecalin (XVIII) 1·8 g., b. p. 75°/14 mm., $n_D^{17\cdot 6°}$ 1·4702, $d_{4°}^{17\cdot 6°}$ 0·8684, $[R_L]_D$ 48·91 (calc., 48·60). This hydrocarbon was treated with warm 2% potassium permanganate solution for 1 hour, refluxed over potassium for 6 hours, and distilled. The physical properties (p. 472) were only slightly changed (Found: C, 86·2; H, 13·2. Calc. for $C_{11}H_{20}$: C, 86·75; H, 13·25%).

Oxidation of cis-9-*Methyl*-Δ^2-*octalin*.—6 G. of the hydrocarbon were shaken mechanically with 20 g. (25% excess) of potassium permanganate in 3% solution and 4·2 g. of sodium carbonate. After 4 hours the solution was decolourised with sulphur dioxide, evaporated to small bulk, acidified, and extracted with ether (five hand extractions). Removal of the solvent from the extract left an oil, which rapidly solidified. After purification through sodium bicarbonate, 3·1 g. of solid acid were obtained, which were crystallised several times from boiling water, forming white opaque nodules, m. p. 160—163° [Found: C, 61·6; H, 8·3; equiv., 106·9. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·3%; equiv. (dibasic), 107·0]. This substance is mainly cis-1-*methyl*cyclo*hexane*-1 : 2-*diacetic acid* (XX).

The aqueous solution from the hand extractions was extracted continuously with ether for

several days. The extract on removal of the ether left a gum, which deposited a few crystals of an acid very soluble in water. This crystallised by evaporation of its ethereal solution in beautiful needles, m. p. 103°, and was not oxalic acid. Insufficient was obtained for identification. 5 G. of the uncrystallisable gum from several oxidations were esterified in the usual way. Fractionation of the ethyl ester so obtained yielded (i) 1·3 g., b. p. 128°/12 mm., probably ethyl adipate (Found: C, 59·3; H, 8·7. Calc. for $C_{10}H_{18}O_4$: C, 59·4; H, 8·9%); (ii) 2·2 g., b. p. 158—170°/12 mm., from which 0·4 g. of ester, b. p. 158°/16 mm., was isolated. This appears to be mainly *ethyl* 1-*methyl*cyclo*hexane*-1 : 2-*dicarboxylate* (Found: C, 64·8; H, 8·9. $C_{13}H_{22}O_4$ requires C, 64·4; H, 9·1%); on hydrolysis it gave a mixture of acids, m. p. 138—171°. The higher fractions of (ii) yielded 0·6 g. of ester, b. p. 178°/18 mm., which was mainly the *homologue* of the foregoing ester, but yielded a mixture of acids on hydrolysis (Found: C, 65·1; H, 9·0. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%).

The crude *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid, m. p. 160—163°, was heated with a crystal of baryta in a fused-salt bath to 280—285°; carbon dioxide and a ketone were then evolved. The distillate was washed with alkali, and the ketone converted into the *semicarbazone*, which formed readily in the cold. Yield 1·7 g., m. p. 221—223° (Found: C, 63·3; H, 8·8. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·2%). Repeated crystallisation of this from alcohol gave a very small amount of a less soluble semicarbazone (probably *trans*-), m. p. 238°, and a more soluble isomeride (probably *cis*-), m. p. 220°. The residual barium salt from the ketonisation was boiled with a little dilute hydrochloric acid. The filtered solution on cooling deposited 0·1 g. of an acid, m. p. 188—194°, probably trans-1-*methyl*cyclo*hexane*-1 : 2-*diacetic acid*, which formed flattened needles from water, m. p. 194—196° (Found: C, 61·2; H, 8·4. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·3%). This, heated with baryta, gave a ketone which yielded a semicarbazone, m. p. 238—239° after one crystallisation from methyl alcohol, identical with that, m. p. 238°, described above.

The mixed semicarbazones from the ketonisation, m. p. 224—228°, were hydrolysed with oxalic acid, and the 9-*methyl*-2-*hydrindanone* distilled in steam and isolated by means of ether. Two separate regenerations gave the following results: yield 72, 76%; b. p. 109°/20 mm., 219°/760 mm.; $n_D^{17.5°}$ 1·4791, 1·4792; $d_{4°}^{17.5°}$ 0·9811, 0·9798; $[R_L]_D$ 43·97, 44·05 (calc., 43·99) (Found: C, 79·3; H, 11·0. $C_{10}H_{16}O$ requires C, 78·95; H, 10·5%). The normal molecular refractivity agrees with the *cis*-configuration. The introduction of the 9-methyl group into 2-hydrindanone brings about a fall in the physical constants. The physical measurements given above were carried out on a supercooled sample: the ketone readily set to a glassy solid, which had a low but indefinite m. p. It had a pleasant, rather camphoraceous, odour.

0·5 G. of the regenerated ketone was slowly added to 0·6 c.c. of boiling concentrated nitric acid under reflux. After addition of 2 c.c. of water, the mixture was boiled for 30 minutes and left over caustic soda in a desiccator. Some solid separated rapidly and was removed. The mother-liquor deposited an oil on evaporation, which was taken up in water and again evaporated in a vacuum desiccator, more solid being formed. Total yield, 0·21 g.; m. p. 135—152° after one crystallisation from water [Found: equiv., 99·3. Calc. for $C_8H_{14}(CO_2H)_2$: equiv., 100]. Fractional crystallisation from water yielded a less soluble acid in prismatic needles, m. p. 173—175° alone or mixed with cis-1-*methyl*cyclo*hexane*-1-*carboxylic*-2-*acetic* acid (m. p. 175°; see p. 473) (Found: C, 60·2; H, 8·6. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·1%). The more soluble fractions yielded a very small quantity of prismatic crystals of the trans-*isomeride*, m. p. 162—164° alone or mixed with synthetic material (m. p. 163—164°; see p. 473). The m. p. was depressed by admixture with *cis*-1-methyl*cyclo*hexane-1 : 2-dicarboxylic acid (m. p. 160°). Oxidation of the ketone with potassium permanganate in acetone led to gross decomposition.

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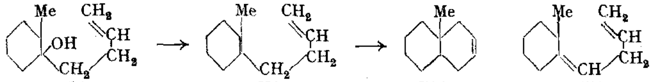
113. *Fused Carbon Rings. Part VIII. The Dehydration of 2-Methyl-1-Δ^3'-butenyl*cyclo*hexanol.*

By D. C. HIBBIT, R. P. LINSTEAD, and A. F. MILLIDGE.

A STUDY of the dehydration of 2-*methyl*-1-Δ^3'-*butenyl*cyclo*hexanol* (I), isomeric with 1-methyl-2-Δ^3'-butenyl*cyclo*hexanol [(XI) in the preceding paper], has given results of some theoretical interest. The alcohol (I) is readily obtained by the interaction of butenyl-

magnesium bromide with 2-methyl*cyclo*hexanone. When heated with phosphoric acid at 130° under the conditions which rapidly cyclise its isomeride, it yields a mixture of hydrocarbons consisting mainly of the monocyclic diene, *2-methyl-1-$\Delta^{3'}$-butenyl*cyclo*hexene* (II). By prolonging the time of heating, more cyclisation occurs with the formation of *cis*-9-methyl-Δ^2-octalin (III). This octalin is formed to the exclusion of the diene when the alcohol (I) is heated at 150° with a mixture of phosphoric acid and its anhydride.



(I.) (II.) (III.) (IV.)

The product resembled in its physical properties the *cis*-9-methyloctalin described in Part VII (preceding paper) and on oxidation yielded the same two 1-methyl*cyclo*hexane-1 : 2-diacetic acids. Both these acids (m. p.'s 163° and 192°) yielded neutral esters on rapid esterification with methyl-alcoholic sulphuric acid and it is therefore improbable that either of them contains a tertiary carboxyl group (contrast 1-methyl-Δ^2-*cyclo*hexene-1 : 2-dicarboxylic acid, p. 483). This supports the Δ^2-structure for the octalin. The 8-methyl-2-hydrindanone obtained on cyclisation was practically pure *cis*-compound; it gave a semicarbazone, m. p. 219°, and on oxidation with nitric acid *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid, identical with that of Part VII. The isomeric *trans*-acid could not be detected. These results agree with the *cis*-9-methyloctalin structure for the original hydrocarbon, but it is necessary to make the same reservations as to the possible presence of 8-methyloctalin as in the preceding paper.

The results described here and in Part VII present some interesting contrasts with those obtained by Bogert, Davidson, and their collaborators in their important study of the *cyclo*-dehydration of alcohols containing a carbon chain of 5—7 carbon atoms terminated by a phenyl group (*J. Amer. Chem. Soc.*, 1934, **56**, 185, 959; 1935, **57**, 151). These substances yield tetralins and/or indanes on treatment with sulphuric or phosphoric acid. Although a strict comparison is not yet possible, it appears that there is a greater latitude in the type of structure capable of cyclising when an aromatic ring is involved. The formation of a *cyclo*pentane ring in the case of the indanes has as yet no parallel among purely hydroaromatic compounds.

There appears to be no doubt that the formation of 9-methyloctalin from 2-methyl-1-butenyl*cyclo*hexanol passes through the stage of the diene (II). The cyclisation of this diene by phosphoric acid at 130° is slow compared with that of 1-methyl-2-butenyl*cyclo*hexanol. Hence it is very probable that the formation of octalin from the latter involves a direct *cyclo*-dehydration. The facts could, however, be explained if 1-methyl-2-butenyl*cyclo*hexanol were dehydrated to (II), which cyclised readily, whereas its isomeride (I) yielded the diene (IV), which could only yield an octalin after isomeric change, *e.g.*, to (II). The rate-determining process would then be the change (IV) $\longrightarrow$ (II). This explanation, although unlikely, is not excluded by the experimental evidence. It is of interest that in the aromatic series Bogert and Davidson (*loc. cit.*) conclude that both cyclisation through the diene stage and direct *cyclo*-dehydration can occur, but that the former is the usual mechanism.

The most promising result from the dehydration of cyclic butenyl compounds is that it leads to the formation of decalins of the same configuration (*cis*-) as that present in many dicyclic sesquiterpenes (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1171). The application of the new method to the synthesis of substances related to these and to the sex-hormones is in hand; also the cyclisation of analogous substances without a potential angular methyl group.

Experimental.

An ethereal solution of 56 g. (0·5 mol.) of 2-methyl*cyclo*hexanone was added to the well-stirred Grignard reagent prepared from 67 g. (0·5 mol.) of Δ^3-butenyl bromide and 12 g. of magnesium in 400 c.c. of dry ether. The mixture was refluxed over-night and poured on ice and

acetic acid, and the aqueous solution extracted with ether. The ethereal solution was washed with sodium carbonate, dried, and evaporated. After the recovery of some unchanged ketone, *2-methyl-1-Δ³′-butenyl*cyclo*hexanol* (I) distilled at 98—108°/18 mm.; after redistillation it had b. p. 104—108°/18 mm., $n_D^{16.5°}$ 1·4784, $d_{4°}^{16.5°}$ 0·9239, $[R_L]_D$ 51·56 (calc., 51·86) (Found: C, 78·0; H, 11·5. $C_{11}H_{20}O$ requires C, 78·5; H, 11·9%).

Dehydration. When 5 g. of the alcohol were shaken with 24 c.c. of syrupy phosphoric acid, the temperature rose to about 40°. The mixture was heated at 130° (oil-bath) for 1 hour, and the product isolated as described in the preceding paper. 4 G. (90%) of *hydrocarbon* (II) were obtained, b. p. 75—78°/10 mm., which after distillation over sodium had $n_D^{15.5°}$ 1·4853, $d_{4°}^{15.5°}$ 0·8769, $[R_L]_D$ 49·10 (calc. for 1 |=, 48·13; for 2 |=, 49·86) (Found: C, 87·6; H, 12·0. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%). The bromine addition was 292 g. per g.-mol. (calc. for two double bonds, 320), but we do not regard this as trustworthy. A similar dehydration for 2 hours at 140° yielded, after distillation over sodium, 3 g. of mainly dicyclic hydrocarbon, b. p. 82—84°/14 mm., $n_D^{16.5°}$ 1·4903, $d_{4°}^{16.5°}$ 0·8950, $[R_L]_D$ 48·49.

15 G. of 2-methyl-1-Δ³′-butenyl*cyclo*hexanol were heated at 140—150° for 5 hours with 65 c.c. of phosphoric acid (*d* 1·75) and 10 g. of phosphoric oxide. The product, isolated as before and distilled over sodium, had b. p. 84—86°/14 mm., $n_D^{15°}$ 1·4939, $d_{4°}^{15°}$ 0·9053, $[R_L]_D$ 48·22, and was essentially *cis*-9-methyloctalin. Yield, 9 g. (Found: C, 87·8; H, 11·9. Calc. for $C_{11}H_{18}$: C, 87·9; H, 12·1%). 6 G. of the methyloctalin were shaken over-night with 20 g. of potassium permanganate and 7 g. of sodium carbonate in 700 c.c. of water and the acids formed by oxidation were isolated as described in the preceding paper. After crystallisation from very dilute acetic acid, 1·4 g. of an acid, m. p. 156—162°, were obtained which on further crystallisation gave an almost pure acid, m. p. 163—165°, and an inseparable mixture, m. p. 165—175°. The m. p. of the former was not depressed by admixture with the *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (m. p. 160—163°) described in Part VII. 0·4 G. of the acid of m. p. 163—165° was boiled for an hour with 10 c.c. of methyl alcohol and 1 c.c. of sulphuric acid. The *dimethyl* ester (0·3 g.) was separated in the usual manner, b. p. 122—125°/1 mm. (Found: C, 64·2; H, 8·8. $C_{13}H_{22}O_4$ requires C, 64·4; H, 9·1%). There was no acid fraction. Hydrolysis of the dimethyl ester re-formed an acid of m. p. 161—163°.

2·35 G. of *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (m. p. 163—165°) were heated with 0·1 g. of baryta to 280—290°. The 8-methyl-2-hydrindanone (1·1 g.) was isolated as before, b. p. 98—100°/12 mm., and rapidly set to a glass. The semicarbazone melted at 218—219° alone and at 220° in admixture with that described in Part VII. The ketone (0·45 g.) when oxidised as before gave 0·3 g. of crude acid, which on crystallisation from water yielded a comparatively insoluble acid, m. p. 170—174°, not depressed on admixture with *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid, m. p. 174°.

The residue from the ketonisation to 8-methyl-2-hydrindanone yielded an acid, m. p. 185—190°, which formed radiating clusters of rhombs from dilute acetic acid, m. p. 191—193° alone or mixed with the corresponding acid of Part VII. When this was esterified with methyl-alcoholic sulphuric acid as before, it gave an equal weight of a neutral ester and no acid ester. Hydrolysis of the ester regenerated the original acid, m. p. 193—194°.

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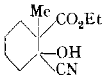
114. *Fused Carbon Rings. Part IX. The Synthesis of Stereoisomeric 1-Methyl*cyclo*hexane-1 : 2-dicarboxylic Acids and of Various Methyl*cyclo*hexanecarboxylicacetic Acids. The Influence of the Angular Methyl Group on the Stability of their Anhydrides.*

By R. P. LINSTEAD and A. F. MILLIDGE.

THE experiments now described were carried out with a view to the preparation of reference substances for the determination of the structure of the dicyclic compounds mentioned in the previous papers. The study of these substances throws some light on the effect of a 1-methyl group on the stability of the *cis*- and the *trans*-forms of cyclic 1 : 2-acids and their anhydrides. The following acids have been prepared:

Acid.	M. p.
cis-1-Methyl*cyclo*hexane-1 : 2-dicarboxylic	160°
trans- ,, ,,	210
cis- ,, -1-carboxylic-2-acetic	175
trans- ,, ,,	164
? *cis*- ,, -2-carboxylic-1-acetic	172
? *trans*- ,, ,,	132
,, ,, -3-acetic (2 forms)	165 and 140

1-Methyl*cyclo*hexane-1 : 2-dicarboxylic acid, closely related in structure to deoxycantharidinic acid, has been synthesised in both forms by a method resembling the Küster synthesis of hæmatinic acid. 2-Methyl*cyclo*hexanone-2-carboxylic ester was converted into the *cyanohydrin* (I), which was unusually stable, in harmony with Lapworth and Manske's views on the effect of α-alkylation (J., 1930, 1976). The corresponding *hydroxy-acid* could not be smoothly dehydrated, but Darzens dehydration of the cyanohydrin readily yielded *ethyl 2-cyano-1-methyl-*Δ^2-cyclo*hexene-1-carboxylate* (II). Hydrolysis of this gave *1-methyl-*Δ^2-cyclo*hexene-1 : 2-dicarboxylic acid* (III), the two carboxyl groups of which differed in the expected way. Fischer–Speier esterification yielded the *2-carbomethoxy*-compound (IV), and partial hydrolysis of the *dimethyl* ester, obtained through the silver salt, the 1-*carbomethoxy*-compound (V).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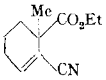
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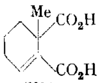
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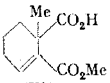
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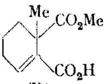
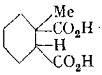
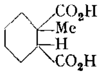

(V.)

The unsaturated cyano-ester (II) was not reduced by aluminium amalgam, but the dimethyl ester of (III) could be reduced catalytically to a mixture of the *cis*- and the *trans*-form of the corresponding saturated ester. Hydrolysis of this yielded a mixture of the acids (VI) and (VII). This was heated with hydrochloric acid at 180°, and fractional crystallisation then yielded the α-acid, m. p. 160°.

Treatment of the mixture of methyl esters with potassium (Hückel and Goth, *Ber.*, 1925, **58**, 447) yielded an ester, which was hydrolysed to an acid, m. p. 200°. Fractional crystallisation of this gave the pure β-acid, m. p. 210°.

(VI.)


(VII.)

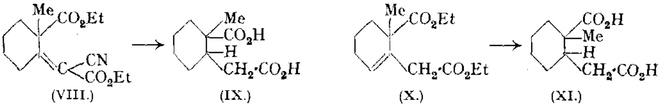
Optical methods cannot be used for the orientation of these acids, which are both racemates. Their configurations are therefore based on analogy and are probable but not certain. The α-form (m. p. 160°) is considered to be the *cis*-acid for the following reasons : (i) There is a general resemblance in properties between the α- and the β-acid and *cis*- and *trans*-hexahydrophthalic acid (m. p.'s 190° and 220°) respectively. The *anhydride* of the α-acid is amorphous and low-melting like that of *cis*-hexahydrophthalic acid, whereas the anhydrides of the β-acid and of *trans*-hexahydrophthalic acid are crystalline and melt at 80° and 140° respectively. (ii) When the anhydride of the α-acid is heated at 240°, it yields 21% of the isomeric anhydride. A similar mixture (30% β-) is obtained by the action of acetic anhydride on the original mixture of acids. By analogy with hexahydrophthalic acid, the acid with the more stable anhydride is the *cis*-form.

The mixture of acids obtained through the equilibration of the esters with potassium contains only 60% of the *trans*-compound, and in comparison with the results of Hückel and Goth (*loc. cit.*) the methyl group has to some extent stabilised the *cis*-form. The action of hydrochloric acid is anomalous : this process usually yields *trans*-acids, but in the present case gives a mixture containing 85% of the *cis*-acid. Ingold (J., 1925, **127**, 398) observed that the conversion of the similarly substituted *cis*-1-methyl*cyclo*propane-1 : 2-dicarboxylic acid into the *trans*-form by hydrochloric acid was only partial. We take the

evidence of configuration from the anhydride equilibrium to be more reliable than that from the relative stabilities to hydrochloric acid.

Both forms of 1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid have been synthesised from 2-methyl*cyclo*hexanone-2-carboxylic ester. Owing to the inhibiting effect of the two α-substituents the reactivity of the ketone group is lowered, and it fails to condense with cyanoacetic ester under the usual conditions (Barrett, Cook, and Linstead, J., **1935**, 1065). In the course of an investigation which one of us is carrying out with Drs. Newitt and Sapiro of this College, it has been found that this condensation can be effected at very high pressures. An account of this work will follow later. The product of the reaction was of the usual type (VIII) and on reduction with aluminium amalgam and hydrolysis yielded *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid (IX), m. p. 174—175°. The *cis*-configuration is assigned to this acid by analogy with previous results; for example, the unsaturated cyano-esters obtained from *cyclo*pentanone-2-acetic ester and *cyclo*hexanone-2-β-propionic ester yield mainly compounds of the *cis*-series by similar treatment (Linstead and Meade, J., 1934, 935; Barrett, Cook, and Linstead, *loc. cit.*). The present acid was identical with that obtained by the oxidation of 8-methyl-2-hydrindanone (preceding papers).

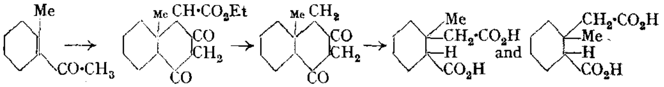
While this work was in progress Chuang, Tien, and Huang (*Ber.*, 1935, **68**, 864) described a 1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid, m. p. 163—164°, obtained from the same keto-ester by the Reformatsky condensation with bromoacetic ester, dehydration of the product to the unsaturated ester (X, or an isomeride), reduction, and hydrolysis. We have confirmed this result. The acid is isomeric and not identical with that of m. p. 174—175°, and is identical with that obtained by Hibbit and Linstead in small quantity by the oxidation of 8-methyl-2-hydrindanone (Part VII). The *trans*-configuration (XI), which follows by exclusion, falls into line with the orientation of *cyclo*pentane-1 : 2-diacetic acid. When this is made from *cyclo*pentanone-2-acetic ester by the Reformatsky route, the product may contain a considerable proportion of *trans*-material (Linstead and Meade, *loc. cit.*; Hückel, Goth, and Demmler, *Ber.*, 1934, **67**, 2102).



(VIII.) (IX.) (X.) (XI.)

The acids (IX) and (XI) do not appear to be interconvertible by the usual methods, in agreement with the absence of a >CH·CO_2H group in the ring.

To consolidate the whole position we have prepared the *cis*- and the *trans*-form of 1-methyl*cyclo*hexane-2-carboxylic-1-acetic acid and two of the four forms of 1-methyl-*cyclo*hexane-2-carboxylic-3-acetic acid. While the work was in progress the preparation of one form of the first of these acids was reported by Clemo and Dickenson (J., **1935**, 735), who used the method of Ruzicka, Koolhaas, and Wind (*Helv. Chim. Acta*, 1931, **14**, 1161).

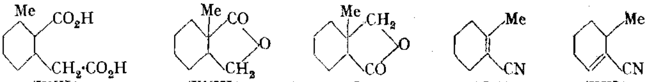


(XII.) (XIII.) (XIV.) (XV.) (XVI.)

We found that hypobromite oxidation of the mixture of 9-methyldecalin-2 : 4-diones (XIV), obtained by the hydrolysis of (XIII), yielded a mixture of two acids (XV, XVI), melting at 171—172° and 131—132°, the former of which was isolated by Clemo and Dickenson. These acids are interconvertible and are therefore related as *cis*- and *trans*-isomerides. Clemo and Dickenson rightly point out that Ruzicka's work does not exclude the possibility that in the condensation of acetylmethyl*cyclo*hexene (XII) with sodiomalonic ester a migration of the double bond might precede addition; in which case the diketodecalin

derivatives would contain an 8- instead of a 9-methyl group and the acid(s) obtained on oxidation would have formula (XVII). Their experiments on the dehydrogenation of the hydrocarbon derived from (XIV), however, favour the 9-methyl arrangement.

We have confirmed Ruzicka's interpretation of the addition (XII ⟶ XIII) by the synthesis of the higher-melting form of 1-methyl*cyclo*hexane-2-carboxylic-1-acetic acid from its lower homologue by a process corresponding to Haller's synthesis of homocamphoric acid. *cis*-1-Methyl*cyclo*hexane-1 : 2-dicarboxylic acid anhydride was reduced to the corresponding lactone, probably a mixture of (XVIII) and (XIX), by means of sodium and alcohol. The lactone was heated with potassium cyanide, and the acidic product hydrolysed with hydrochloric acid to 1-methyl*cyclo*hexane-2-carboxylic-1-acetic acid, m. p. 172°, identical with that prepared from 9-methyldecalindione.



(XVII.) (XVIII.) (XIX.) (XX.) (XXI.)

The fact that the product was a 1-acetic acid (XV or XVI) and not a 2-acetic acid (IX or XI) shows that the lactone which reacted was the form (XIX). Camphoric anhydride yields mainly α-campholide (corresponding to XVIII) on reduction. In view of this it seems probable that our lactone was a mixture of (XVIII) and (XIX), the latter being more reactive towards potassium cyanide. From the work of Hückel *et al.* (*Annalen*, 1934, **514**, 240) the lactones are the *cis*-modifications.

The configurations of the 1-methyl*cyclo*hexane-2-carboxylic-1-acetic acids are uncertain. Clemo and Dickenson (*loc. cit.*) take the 172°-acid to be the *cis*-form, presumably by analogy with the reported oxidation of decalin-1 : 3-dione to *cis*-*cyclo*hexane-1-carboxylic-2-acetic acid (Kon and Qudrat-i-Khuda, J., 1926, 3071). It has been shown, however, that this oxidation actually yields the *trans*-acid (Barrett, Cook, and Linstead, *loc. cit.**). It is known that Ruzicka, Koolhaas, and Wind's diketone (XIV) gave a 9-methyldecalin on Clemmensen reduction, from which the *trans*-isomeride was isolated by fractionation. Our preparations of this diketone yielded on oxidation the 172°- and the 132°-acid in the proportion of about 7 : 3 (the actnal ratio was probably nearer equality than this, because the lower-melting acid is harder to isolate). The evidence from this source is thus indecisive, but perhaps favours the *trans*-configuration for the 172°-acid. Other considerations, however, lead to the opposite view. The 172°-acid has been prepared from a *cis*-lactone (although this evidence is rendered less decisive by the high temperature—280°—required for the fission of the lactone ring). When the 172°-acid is heated with hydrochloric acid at 200°, it changes to the extent of 92% into the 132°-acid. Chuang, Ma, and Tien (*Ber.*, 1935, **68**, 1946) have examined the corresponding derivatives of *cyclo*pentane. By the oxidation of an 8-methylhydrindandione (which on general stereochemical grounds should be *cis*-) they obtained a *cis*-1-methyl*cyclo*pentane-2-carboxylic-1-acetic acid, with a stable anhydride. This was converted almost completely into the *trans*-isomeride by hydrochloric acid at 200°. In spite of the anomalous behaviour of 1-methyl*cyclo*hexane-1 : 2-dicarboxylic acid, it is reasonable to suppose that the *cyclo*pentane and the *cyclo*hexane series would behave similarly in this reaction; in which case the 172°-acid would be *cis*-. On the whole we regard this as the more probable configuration.

Both forms of the acid gave anhydrides. When the anhydride of the 172°-acid was heated to 250°, it yielded a mixture containing 55% of its isomeride, which was separated

* A recent paper by Chuang and Tien (*Ber.*, 1936, **69**, 25) describes the oxidation of pure *trans*-decalin-1 : 3-dione to *trans*-*cyclo*hexane-1-carboxylic-2-acetic acid, but makes no reference to the prior work of Barrett, Cook, and Linstead. Chuang and Tien's experiments indicate that at least a considerable proportion of the primary product in reactions such as (XII ⟶ XIII) has a *cis*-locking of the 6-membered rings. This *cis*-material may subsequently change to *trans*- during hot alkaline hydrolysis (as of XIII ⟶ XIV). This is surprising in view of the fact that the additions are carried out in the presence of sodium ethoxide, which would be expected to yield the stable *trans*-α-decalone system.

into the acids of m. p. 172° and 132°. When the *cis*-acid was heated to 350° with baryta, it yielded anhydride but no ketone, showing that the usual rules hold.

Two forms of 1-*methyl*cyclo*hexane-2-carboxylic-3-acetic acids* (XVII) were synthesised by the addition of sodiomalonic ester to the unsaturated nitrile obtained by dehydration of 2-methyl*cyclo*hexanone cyanohydrin. This was presumably a mixture of the Δ^1- and the Δ^6-form (XX and XXI), but only the latter reacted and the yield of additive product was small. The reaction is analogous to that studied by Perkin (J., 1896, **69**, 1460), who found that αββ-trimethylacrylic ester did not condense with ethyl sodiomalonate, whereas the isomeric α-*iso*propylacrylic ester reacted. The mixture obtained by hydrolysing the condensation product was separated into two isomeric forms of (XVII). One of these, m. p. 165°, yielded the other, m. p. 140°, when heated with hydrochloric acid at 190°. These acids probably contain the carboxyl group respectively in the *cis*- and the *trans*-position to the acetic acid group, the orientation of the latter to the methyl group being unknown.

As far as can be seen at present, the angular methyl group tends to stabilise the *cis*-forms of *o*-dicyclic systems. This is shown by the following figures :

Acids.	% *cis*-Anhydride at equilibrium.	Reference.
{ *cyclo*Hexane-2-carboxylic-1-acetic	25	Windaus, Hückel, and Reverey, *Ber.*, 1923, **56**, 91.
{ 1-Methyl ,, ,,	*ca.* 50 *	This paper.
{ *cyclo*Pentane-2-carboxylic-1-acetic	86	Cook and Linstead, J., 1934, 956.
{ 1-Methyl ,, ,,	*ca.* 100	Chuang, Ma, and Tien, *loc. cit.*

* Independent of which configuration is finally established.

This also appears in the tendency for the *cis*-form of 9-methyldecalindione (XIV) to persist after alkaline hydrolysis of the keto-ester (XV). The stabilisation of the *cis*-form is in agreement with Hückel's theoretical views (" Fortschritte," 1927, **19**, Heft 4, 61). It is uncertain whether the anhydride equilibrium of the 1-methyl*cyclo*hexane-1 : 2-dicarboxylic acids constitutes an exception to this.

Attempts at the preparation of methyl*cyclo*hexanecarboxylicacetic acids by the addition of butadiene to derivatives of α- and β-methylglutaconic acids were fruitless. The preparation of α-methylglutaconic acid has been improved.

Experimental.

1-*Methyl*cyclo*hexane*-1 : 2-*dicarboxylic Acids.*—Ethyl 2-methyl*cyclo*hexanone-2-carboxylate was prepared in 90—95% yield by the action of methyl iodide on sodio*cyclo*hexanone-2-carboxylic ester in boiling benzene. Hydrogen cyanide from 50 g. of potassium cyanide (Wade and Panting, J., 1898, **73**, 256), cooled in a freezing mixture, was treated with a few drops of potassium cyanide solution and then with 50 g. of the methylated keto-ester in drops. The mixture was kept in ice over-night, the alkali neutralised with sulphuric acid, and the excess of hydrogen cyanide removed by suction. *Ethyl* 1-*cyano*-2-*methyl*cyclo*hexanol*-2-*carboxylate* (I) distilled at 148—149°/12 mm. as a colourless viscous liquid; yield, 90—95% (Found : C, 63·0; H, 8·3. $C_{11}H_{17}O_3N$ requires C, 62·6; H, 8·2%). It suffers very little decomposition on distillation or on standing in glass vessels at room temperature for a few days.

10 G. were shaken in the cold for 3 days with 60 c.c. of concentrated hydrochloric acid. The mixture was then boiled for 24 hours and evaporated to dryness under reduced pressure. The residue was freed from neutral matter by dissolution in aqueous sodium carbonate and extraction with ether, and was then acidified and extracted thoroughly with ether. 2-*Methyl*-cyclo*hexanol*-1 : 2-*dicarboxylic acid* was isolated from the extract in 60% yield, m. p. 166—167° after crystallisation from acetone and light petroleum [Found : C, 53·5; H, 6·9; equiv., 102. $C_9H_{14}O_5$ requires C, 53·4; H, 7·0% ; equiv. (dibasic), 101]. The acid slowly decolourises alkaline permanganate. If the preliminary shaking with hydrochloric acid is omitted in the hydrolysis of the cyanohydrin, there is much fission to 2-methyl*cyclo*hexanone and the yield falls to 30%. When the acid was boiled with acetic anhydride, it yielded the anhydride of the acetoxy-acid (m. p. 86—87° ; from light petroleum) which by the action of water or dilute alkali (followed by acidification) yielded 2-*acetoxy*-1-*methyl*cyclo*hexane*-1 : 2-*dicarboxylic acid*. This, crystallised from ethyl acetate and light petroleum, had m. p. 168°, depressed by admixture with the hydroxy-acid [Found : C, 54·4; H, 6·6; equiv., 122·5. $C_{11}H_{16}O_6$ requires C, 54·1; H, 6·6% ; equiv. (dibasic), 122].

To an ice-cold mixture of 42 g. (0·2 mol.) of the cyanohydrin of 2-methyl*cyclo*hexanone-carboxylic ester and 32 g. (0·4 mol.) of dry pyridine, 48 g. (0·4 mol.) of thionyl chloride were slowly added with shaking. White pyridine salts separated and the mixture turned brown. It was heated on the steam-bath for an hour, cooled, treated with ice and hydrochloric acid, and extracted with ether. The extract was filtered, shaken with caustic soda solution and then with water, and dried over sodium sulphate. The residue from the ether yielded a low fraction containing dissolved sulphur, and *ethyl* 2-*cyano*-1-*methyl*-Δ^2-cyclo*hexene*-1-*carboxylate* (II), b. p. 140—141°/9 mm.; yield, 90—95% (Found: C, 68·1; H, 7·7. $C_{11}H_{15}O_2N$ requires C, 68·3; H, 7·8%). This was hydrolysed by boiling with an excess of concentrated hydrochloric acid. The acid (III) separated even while hot and was filtered off after the mixture had been cooled and diluted. Yield, 85—90%.

1-*Methyl*-Δ^2-cyclo*hexene*-1 : 2-*dicarboxylic acid* (III) is soluble in cold water to about 0·2% and crystallised from water or, better, acetic acid in rhombic prisms, m. p. 229—230° (efferv.) (Found: C, 58·5; H, 6·3. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%). The *anhydride* was obtained by boiling the acid with acetic anhydride for 2 hours and removing the excess with the aid of the pump. The solid residue formed plates, m. p. 67—68°, from ether–light petroleum (Found: C, 65·2; H, 6·0. $C_9H_{10}O_3$ requires C, 65·0; H, 6·1%). The acid has a tendency to form an acid silver salt and the *disilver* salt was best prepared by slowly adding a neutral solution of the ammonium salt to a stirred excess of silver nitrate solution and continuing the stirring overnight. Even so the salt was somewhat deficient in silver (Found: Ag, 50·8. $C_9H_{10}O_4Ag_2$ requires Ag, 53·8%). The *dimethyl* ester, b. p. 140°/11 mm., was obtained by boiling the silver salt with methyl iodide in ether for 24 hours. It was isolated in the usual manner and freed from a little monoester with sodium carbonate. It could also be prepared by Fischer–Speier esterification for 10 days on the water-bath (Found: C, 62·1; H, 7·5. $C_{11}H_{16}O_4$ requires C, 62·2; H, 7·6%). When the acid (2 g.) was boiled for 3 hours with 50 c.c. of 5% methyl-alcoholic sulphuric acid, it yielded 2-*carbomethoxy*-1-*methyl*-Δ^2-cyclo*hexene*-1-*carboxylic acid* (IV), isolated by means of ether in the usual manner. This solidified fairly rapidly and formed small plates, m. p. 112—114°, from acetone–light petroleum [Found: C, 60·2; H, 6·9; equiv., 196. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%; equiv. (monobasic), 198]. 1·5 G. of the dimethyl ester were refluxed for 3 hours with 0·4 g. of caustic potash in 10 c.c. of aqueous methyl alcohol. The alcohol was removed, water added, and any unchanged di-ester removed with ether. The solution was then acidified and extracted thoroughly with ether. The extract was dried over sodium sulphate, and the solvent removed. The residue of 1-*carbomethoxy*-1-*methyl*-Δ^2-cyclo*hexene*-2-*carboxylic acid* (V) solidified rapidly and formed a microcrystalline powder, m. p. 119—120°, from acetone–light petroleum (Found: C, 60·3; H, 6·9%; equiv., 197). A mixture of the two isomeric monomethyl esters melted below 100°.

40 G. of the dimethyl ester were hydrogenated in alcoholic solution with 0·3 g. of Adams's catalyst, the theoretical quantity of hydrogen being absorbed in 6 days. The solution was filtered, the solvent removed, and the mixture of saturated esters isolated in almost theoretical yield as a fraction of b. p. 122—129°/9 mm. When this was boiled for 15 hours with concentrated hydrochloric acid, white crystals separated in the hot, and were filtered off from the cooled solution. Yield, almost theoretical; m. p. indefinite, about 170°. 3 G. of the mixture of saturated dimethyl esters were added to 0·5 g. of "molecular" potassium, suspended in 15 c.c. of dry ether. The mixture was refluxed for 10 hours (which appeared to be necessary for the complete formation of the potassio-compound), cooled, and treated with water and dilute acid. The ethereal solution left 1·5 g. of an ester, b. p. 124—126°/10 mm., and there was a considerable high fraction. Hydrolysis of the ester with hydrochloric acid as before gave an acid, m. p. 200°, which by thermal analysis contained 40% of *cis*-acid (see below). This was the richest source of *trans*-material available and after crystallisation from aqueous acetone to constant m. p. gave the pure trans-*acid* (VII) as clusters of small rhombic prisms, m. p. 210°, or 213° if placed in a bath at 150° (Found: C, 57·8; H, 7·5. $C_9H_{14}O_4$ requires C, 58·0; H, 7·6%). The pure acid is practically insoluble in cold water, but is more soluble in the presence of the *cis*-form.

2 G. of the mixture of acids (m. p. *ca.* 170°) were heated at 190° for 15 hours with 10 c.c. of concentrated hydrochloric acid. There was hardly any charring. The separated acid had m. p. 164° and contained 85% of *cis*-acid. (A similar experiment at 180° scarcely affected the mixture.) Fractional crystallisation of the product from water to constant m. p. yielded the cis-*acid* (VI) as clusters of very small, irregular prisms, m. p. 160° * (Found: C, 57·9; H, 7·4%), very slightly soluble in cold water, soluble in hot. Measured volumes of standard solutions of

* This m. p. is rather indefinite; the acid may still contain some of the *trans*-isomeride.

the two acids were mixed and evaporated to dryness. The m. p.'s of the well-ground solid residues were as follows:

% *cis*-Acid ...	100	90	80	70	60	50	40	30	20	10	0
M. p.	160°	161·5°	165°	189°	195°	198°	200°	203°	205°	207·5°	210°

The m. p. of the lower-melting acid is *not* depressed by admixture with its isomeride. This was also observed with *cis*- and *trans*-*cyclo*pentane-1 : 2-diacetic acid (Barrett and Linstead, J., 1935, 441). The composition of mixtures was determined by comparison.

The pure *trans*-acid was dissolved in an excess of warm acetyl chloride, the excess of reagent removed over caustic potash in a vacuum, and the residual solid trans-*anhydride* crystallised from ether and light petroleum; m. p. 80° (Found: C, 64·0; H, 7·1. $C_9H_{12}O_3$ requires C, 64·2; H, 7·2%). Treatment with dilute alkali, followed by acidification, regenerated the pure *trans*-acid, m. p. and mixed m. p. 210°. The pure *cis*-acid was warmed for an hour with acetic anhydride, the excess of reagent removed, and the product distilled at 144—146°/19 mm. It solidified to an amorphous mass, m. p. 60—65°, and yielded an acid, m. p. 166°, on hydration. Hence this procedure gives an anhydride containing about 80% of the *cis*-form. The anhydride obtained in this way was heated at 240° for an hour, cooled, and treated with aqueous sodium bicarbonate. The solution was decolourised with charcoal, acidified, and evaporated to dryness. The residue was rubbed with water to remove sodium salts, and dried. The acid had m. p. 166—167°, *i.e.*, contained 79% of the *cis*-form. The original mixture of acids (m. p. *ca.* 170°) was similarly treated with acetic anhydride. The product distilled at 132—135°/8 mm., melted at 25—30°, and yielded an acid, m. p. 190° (*ca.* 70% *cis*-), on hydration.

1-*Methyl*cyclo*hexane*-1-*carboxylic*-2-*acetic Acids*.—A mixture of 150 g. of ethyl 2-methyl-*cyclo*hexanone-2-carboxylate, 100 g. of cyanoacetic ester, and 10 g. of piperidine gave no condensation product after 4 months at room temperature (cf. Chuang, Tien, and Huang, *loc. cit.*). The *diethyl 2-methyl*cyclo*hexylidene*-1-*cyanoacetate*-2-*carboxylate* (VIII) obtained by the condensation of a similar mixture under high pressure had b. p. 160—165°/1 mm. (Found: C, 64·3; H, 7·3. $C_{15}H_{21}O_4N$ requires C, 64·4; H, 7·6%). It deposited a small amount of solid, forming long needles from aqueous alcohol, m. p. 85—86°. 2·3 G. of the unsaturated ester were reduced for 24 hours with 4 g. of aluminium amalgam in 100 c.c. of moist ether. The product, isolated in the usual way, was hydrolysed, without purification, with boiling hydrochloric acid for 24 hours. The solution, after decoloration with charcoal, deposited *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid (IX), which crystallised from very dilute acetic acid in clusters of small rhombic prisms, m. p. 174—175° (Found: C, 60·2; H, 8·1. Calc. for $C_{10}H_{16}O_4$: C, 60·0; H, 8·1%). The acid was insoluble in cold, and only moderately soluble in boiling water.*

The diethyl ester of 1-methyl-Δ^2-*cyclo*hexene-1-carboxylic-2-acetic acid (X) was prepared essentially by Chuang, Tien, and Huang's process (*loc. cit.*) except that magnesium was used in place of zinc in the initial condensation. The corresponding saturated ester, obtained by catalytic hydrogenation in methyl alcohol, had b. p. 120—121°/1 mm., and yielded *trans*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid on hydrolysis with boiling concentrated hydrochloric acid; m. p. (crude) 160—161°, 163—164° after recrystallisation from dilute acetic acid, in agreement with the Chinese workers. The acid gave a considerable depression of m. p. when mixed with the isomeride of m. p. 174—175°.

1-*Methyl*cyclo*hexane*-2-*carboxylic*-1-*acetic Acids*.—In the preparation of 1-carbethoxy-9-methyldecalin-2 : 4-dione (XIII) following Ruzicka, Koolhaas, and Wind (*loc. cit.*), most of the unreacted acetylmethyl*cyclo*hexene could be recovered and used for a further condensation. The diketo-ester was isolated as a solid, m. p. 130—131° (cf. Clemo and Dickenson, *loc. cit.*) (Found: C, 66·3; H, 7·8. Calc. for $C_{14}H_{20}O_4$: C, 66·7; H, 8·0%). 20 G. of this were boiled for 24 hours with 75 g. of baryta in 700 c.c. of water. The solution was cooled, acidified, and extracted with ether. The diketone (XIV) was obtained as a glassy resin in 75% yield. To a solution of 10 g. of the diketone in 40 c.c. of 10% aqueous caustic soda, cooled in ice, was added a sodium hypobromite solution made from 25 g. of bromine and 500 c.c. of ice-cold 10% aqueous caustic soda. After an hour at 0°, neutral products were removed by extraction with ether and

* An attempt was made to prepare this acid from the lactone of 1-methyl*cyclo*hexanol-2-acetic acid by treatment with potassium cyanide, followed by hydrolysis. Ethyl *cyclo*hexanone-2-acetate (Chuang and Ma, *Ber.*, 1935, **68**, 872) yielded the lactone when treated with methylmagnesium iodide in 70% yield (b. p. 140—141°/15 mm.; equiv., 156, calc., 154), but the action of cyanide yielded only tarry material.

the solution was saturated with sulphur dioxide and acidified with dilute sulphuric acid. The excess of sulphur dioxide was removed by warming, and the cooled solution extracted continuously with ether for 48 hours. The extract left a semi-solid product, which was boiled with water (charcoal). On evaporation this solution deposited large crystals, which were recrystallised from water to a constant m. p. of 171·5°, in agreement with Clemo and Dickenson (*loc. cit.*). Yield, 4·4 g. 1-*Methyl*cyclo*hexane*-2-*carboxylic*-1-*acetic acid* (?*cis*-, XV) formed prisms, almost insoluble in cold water, sparingly soluble in hot, but more soluble in the presence of the isomeride described below [Found: C, 60·3; H, 8·3; equiv., 100. Calc. for $C_{10}H_{16}O_4$: C, 60·0; H, 8·1%; equiv. (dibasic), 100]. The mother-liquors from this acid were evaporated to dryness, and the sticky residue boiled with water (charcoal). The filtered solution was cooled and scratched, which caused a white crystalline powder to separate, m. p. 129—130°; yield, 1·95 g. After several crystallisations from water, 1-*methyl*cyclo*hexane*-2-*carboxylic*-1-*acetic acid* (?*trans*-, XVI) was obtained as a microcrystalline powder, m. p. 131—132° (Found: C, 60·2; H, 7·9%; equiv., 99). The melting points of mixtures of these two acids were as follows:

% *cis*-	100	90	80	70	60	50	40	30	20	10	0
M. p.	171·5°	168·5°	166·5°	165°	160°	157°	153°	150°	147°	142°	131°

By treatment with acetic anhydride and distillation the acids yielded the corresponding anhydrides, from which the unchanged acids could be regenerated. The anhydride from the "*trans*"-acid was a sticky liquid, b. p. 163—165°/19 mm., that from the "*cis*"-, an amorphous solid, m. p. 50°, b. p. 152—154°/19 mm. The anhydride from the "*cis*"-acid was heated at 240—250° for 2 hours, and the acid recovered in the usual way. It had m. p. 154°, corresponding to about 45% of "*cis*"-form. By fractional crystallisation from water it was separated into the original acid and the "*trans*"-acid, m. p. and mixed m. p. 131°. This proves that the acids are stereoisomerides. The "*trans*"-acid was almost unchanged by hydrochloric acid at 190—200° (15 hours), but the "*cis*"-acid yielded an acid, m. p. 140°, containing over 90% of the "*trans*"-form. When the "*cis*"-acid was heated to 350° with 20% of baryta, the "*cis*"-anhydride distilled.

Synthesis from the Lower Homologue (cf. Haller, *Compt. rend.*, 1896, **122**, 146).—A current of hydrogen was bubbled through *cis*-1-methyl*cyclo*hexane-1 : 2-dicarboxylic anhydride maintained at 270°, and thence through a tube containing a nickel catalyst (Rupe *et al.*, *Helv. Chim. Acta*, 1918, **1**, 452; 1920, **3**, 654) at 220—240°. The only product was a hydrocarbon, b. p. 130—140°, probably 1 : 2-dimethyl*cyclo*hexane. A solution of 19 g. of the anhydride in 250 c.c. of alcohol (calcium-dried) was dropped on 30 g. of sodium at such a rate as to keep the alcohol refluxing gently. The mixture was finally heated on the steam-bath until all the sodium had dissolved, 100 c.c. more alcohol being added. The cooled solution was diluted with water, acidified with hydrochloric acid, and extracted with ether. The extract was washed with sodium bicarbonate solution and water and dried, the solvent removed, and the residue distilled; yield, 7·1 g. (40%) of *lactone* (XVIII and XIX), b. p. 129—132°/12 mm. (Found: C, 69·6; H, 9·2; equiv., 152. $C_9H_{14}O_2$ requires C, 70·0; H, 9·1%; equiv., 154). 1·5 G. of the lactone and 2 g. of powdered potassium cyanide (95% single salt) were heated in a sealed tube at 280—290° for 12 hours. The product was dissolved in water, acidified, and extracted with ether. The residue from the ether was purified in the usual manner through sodium bicarbonate solution, and the cyano-acid hydrolysed with 20 c.c. of boiling concentrated hydrochloric acid for 24 hours. The residue was boiled with water (charcoal), filtered, and allowed to crystallise. The crude acid obtained had m. p. 170°, 172° after crystallisation from water, not depressed by admixture with the acid (m. p. 171·5°) prepared from decalindione (Found: equiv., 100·5. Calc., 100).

1-*Methyl*cyclo*hexane*-2-*carboxylic*-3-*acetic Acids* (XVII).—The cyanohydrin of 2-methyl*cyclo*hexanone was prepared in the same way as the corresponding derivative of methyl*cyclo*hexanonecarboxylic ester (above). It was obtained as a semi-solid mixture of stereoisomerides, b. p. 122—123°/10 mm. (yield, 80—90%), and was dehydrated by thionyl chloride and pyridine by the method already described but without a solvent; yield of tetrahydro-*o*-toluonitrile (XX and XXI) 80%, b. p. 85—86°/10 mm. When benzene was used as a solvent, the dehydration was far from complete. To a cold solution of 15 g. of sodium in 220 c.c. of alcohol were added 50 g. of ethyl malonate, followed by 40 g. of this nitrile. After 4 days at room temperature the mixture was worked up in the usual way. Distillation yielded much unchanged nitrile and 4·5 g. of *diethyl* 2-*cyano*-1-*methyl*cyclo*hexane*-3-*malonate*, b. p. 180—188°/11 mm. (Found: C, 63·7; H, 8·7. $C_{15}H_{23}O_4N$ requires C, 64·0; H, 8·3%). Hydrolysis with boiling

hydrochloric acid for 24 hours in the usual manner yielded a mixture of acids, m. p. 140—150°, with the correct equivalent. After several crystallisations from water this was separated into "*cis*"-1-*methyl*cyclo*hexane-2-carboxylic-3-acetic acid*, plates, m. p. 164—165° (Found: C, 59·8; H, 7·7; equiv., 99·5. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·1%; equiv., 100), and the more soluble "trans"-*isomeride*, a fine crystalline powder, m. p. 138—140° (Found: C, 59·9; H, 7·9%; equiv., 99·2). The barium salt of the "*cis*"-acid was fairly soluble, that of the "*trans*"-acid insoluble, in alcohol. When the acid of m. p. 164—165° was heated with hydrochloric acid at 200° for 12 hours, it yielded the acid of m. p. 138—140°.

Four of the isomeric carboxyacetic acids derived from methyl*cyclo*hexane have similar m. p.'s. These are the *cis*-1-carboxylic-2-acetic (175°), *trans*-1-carboxylic-2-acetic (164°), ?*cis*-2-carboxylic-1-acetic (172°), and ?*cis*-2-carboxylic-3-acetic (165°) acids. These acids depress each other's m. p.'s, which confirms their individuality. The same is true of the ?*trans*-2-carboxylic-1-acetic (132°) and ?*trans*-2-carboxylic-3-acetic (140°) acids.

Attempted Diene Condensations with Derivatives of Methylglutaconic Acids.—The following method for the preparation of α-methylglutaconic acid, based on the work of Thole and Thorpe (J., 1911, **99**, 2196), gave much more satisfactory results than those in the literature. Ethyl αγ-dicarbethoxy-α-methylglutaconate (Thole and Thorpe, *loc. cit.*) was hydrolysed and decarboxylated in two stages. A solution of 86 g. (0·25 mol.) of the ester in 65 c.c. of alcohol was added to sodium ethoxide prepared from 6 g. of sodium and 75 c.c. of alcohol. After an hour at room temperature, the product was poured into a solution of 85 g. (1·5 mols.) of caustic potash in 90 c.c. of alcohol and 30 c.c. of water. The mixture was rapidly cooled to take up the heat of reaction, and was left for 10 days at room temperature. The semi-solid mass was dissolved in water, alcohol was removed by suction, and unchanged ester by ether extraction. The solution was then cooled in ice and made strongly acid, carbon dioxide being evolved. The solution was extracted thoroughly with ether, the extract dried with sodium sulphate, and the solvent removed. The residue, a rather sticky solid, when rubbed with dry ether gave the pure high-melting form of α-methylglutaconic acid as a crystalline powder, m. p. 144—145° (cf. Feist and Pomme, *Annalen*, 1909, **370**, 61; Thole and Thorpe, *loc. cit.*). Yield, 19·5 g. (56%). A further small quantity was recovered from the ethereal washings. The *dimethyl* ester was obtained by the action of 10% methyl-alcoholic sulphuric acid at room temperature for 3 days; b. p. 117°/13 mm. (Found: C, 55·7; H, 6·8. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%).

β-Methylglutaconic acid was obtained from ethyl *iso*dehydracetate by hot alkaline hydrolysis (Feist, *Annalen*, 1906, **345**, 69; Goss, Ingold, and Thorpe, J., 1923, **123**, 348) in 90% yield; m. p. 114—115°. The *dimethyl* ester was prepared through the silver salt or by cold esterification with 10% methyl-alcoholic sulphuric acid; b. p. 109—110°/12 mm. (Found: C, 56·0; H, 6·9%). The enolic anhydride (Bland and Thorpe, J., 1912, **101**, 865) had m. p. 90°.

Butadiene was isolated from "railway hydrocarbon" by the method of Birch (*J. Ind. Eng. Chem.*, 1928, **20**, 474) as the tetrabromide and was regenerated by Thiele's method (*Annalen*, 1899, **308**, 337). A special apparatus was used in which the tetrabromide was continuously extracted by hot alcohol and the extract boiled with zinc dust. The butadiene was freed from alcohol by a water condenser and calcium chloride tube and was condensed in the reaction vessel. The diene from 20 g. of tetrabromide, 4·5 g. of β-methylglutaconic anhydride, and 7 c.c. of benzene were heated at 150° for 3 days. The anhydride was recovered unchanged. Similar experiments with the dimethyl esters of α- and β-methylglutaconic acids gave an amount of condensation product insufficient for examination. The bulk of the ester was recovered and some rubber-like substance was produced.

The work described in this and the preceding paper was carried out during the tenure by one of us (A. F. M.) of a Neil Arnott Studentship of the University of London and a grant from the Department of Scientific and Industrial Research. We thank the Chemical Society and the Royal Society for grants in aid of the work described in this and the two preceding papers.

Imperial College, London, S.W. 7. [*Received, February 19th, 1936.*]

115. *The Apparent Dipole Moments of Benzene,* p-*Dichlorobenzene, Diphenyl, 4 : 4'-Dichlorodiphenyl, and Carbon Disulphide in Polar Solvents.*

By Catherine G. Le Fèvre and Raymond J. W. Le Fèvre.

In this paper are recorded the dielectric constants and densities of solutions in a series of polar solvents of the substances indicated in the title. If the data so obtained can be treated in the usual manner for dipole-moment determinations, the results shown in the following table emerge. The figures under $\mu_{solv.}$ are the values for the solvent as a gas, where these are extant; the other headings have their usual significances. The apparent moments of the five solutes in the various solvents are given, as Debye units, in the penultimate column, and the ratios between the apparent moments of the solutes and the moments of the respective solvents are in the last column.

Solvent.	${}_{T}^{\infty}P$, c.c.	$\epsilon_{solv.}$	$\mu_{solv.}$	${}_{A}P + {}_{E}P$, c.c.	${}_{O}P$, c.c.	$\mu_{app.}$	$\mu_{app.}/\mu_{solv.}$
			(1) *Benzene as solute.*				
C_6H_6	27	2·27	0	27 *	0	0	—
$CHCl_3$	28	4·72 †	1·05	,,	1	*ca.* 0	—
C_6H_5Cl	38	5·61 ‡	1·69 §	,,	11	0·73	0·43
$C_6H_5{\cdot}NO_2$	73	34·89 †	4·23 §	,,	47	1·51	0·36
			(2) p-*Dichlorobenzene as solute.*				
C_6H_6	38	2·27	0	38 **	0	0	—
CCl_4	37	2·23	0	,,	0	0	—
$C_6H_5{\cdot}NMe_2$	48	4·85 ‖	1·6	,,	10	0·70	0·44
C_6H_5Cl	52	5·61	1·69	,,	14	0·82	0·49
$C_6H_5{\cdot}CO_2Et$	53	5·77 ‖	1·8—1·9	,,	15	0·85	0·44
$C_6H_5{\cdot}CN$	91	25·20 †	4·39	,,	53	1·60	0·36
$C_6H_5{\cdot}NO_2$	94	34·89	4·23	,,	56	1·65	0·39
			(3) *Diphenyl as solute.*				
C_6H_6	50	2·27	0	50 ¶	0	0	—
C_6H_5Cl	69	5·61	1·69	,,	19	0·96	0·57
$C_6H_5{\cdot}NO_2$	123	34·89	4·23	,,	73	1·88	0·44
			(4) 4 : 4'-*Dichlorodiphenyl as solute.*				
C_6H_6	66	2·27	0	63 ¶	3	*ca.* 0	—
C_6H_5Cl	77	5·61	1·69	,,	14	0·82	0·48
$C_6H_5{\cdot}NO_2$	146	34·89	4·23	,,	83	2·00	0·47
			(5) *Carbon disulphide as solute.*				
CS_2	21	2·64	0	21 ¶	0	0	—
C_6H_6	23	2·27	0	,,	2	*ca.* 0	—
C_6H_5Cl	26	5·61	1·69	,,	5	0·49	0·29
$C_6H_5{\cdot}NO_2$	51	34·89	4·23	,,	30	1·20	0·28

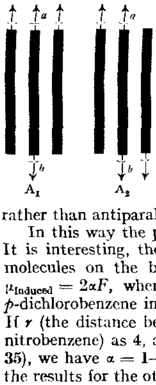
* Errera (*Bull. Acad. roy. Belg.*, 1926, 327).
† Ball (J., 1930, 570).
‡ Sugden (J., 1933, 772).
§ Groves and Sugden (J., 1934, 1094).
‖ Present work.
¶ The $[R_L]_D$ value.
** *I.e.*, the distortion polarisation, taken as 38 c.c. from the measurements of Smyth, Morgan, and Boyce (*J. Amer. Chem. Soc.*, 1928, **50**, 1536) and Errera (*Compt. rend.*, 1936, **182**, 1623; *Physikal. Z.*, 1926, **27**, 764; "Polarisation Diélectrique," Paris, 1928) on the *solid* substance.

The induced moment of the solute is throughout roughly proportional to the *moment*, rather than the dielectric constant, of the solvent (see last column of table); the latter constaut certainly does not have, in these measurements, the large influence indicated by the various empirical and *a priori* equations hitherto advanced.

Discussion.—These results are qualitatively in agreement with a suggestion previously outlined by us (J., 1935, 1747); this depended on the occurrence of regular (graphite-like) units of structure in the liquids, for which (notably aromatic compounds) there seems to be independent physical evidence (cf. Katz, *Z. angew. Chem.*, 1928, **41**, 329; Stewart, *Indian J. Physics*, 1932—3, **7**, 603). The underlying cause of this we suppose to be the operation of van der Waals forces. According to the theories of London (*Z. Physik*, 1930,

63, 245; *Z. physikal. Chem.*, 1931, **11**, *B*, 222), the reciprocal binding energy due to such forces between two atoms at a distance R apart is $E = -C/R^6$, which is approximately equal to $-1{\cdot}36n^{1/2}\alpha^{3/2}\alpha_0^{3/2}E_0/R^6$ (cf. Slater and Kirkwood, *Physical Rev.*, 1931, **37**, 682), in which n is the number of electrons in the outermost shell of the atomic species under consideration. Now, the reciprocal energy of any one atom with respect to a system of others can be obtained by addition of the reciprocal energies with respect to each of these atoms individually. Thus, the reciprocal energy for two molecules is obtained by summation of the mutual energies of all the centres of the first molecule with those of all the centres of the second molecule. The influence of an inverse R^6 term is to make two molecules effecting mutual orientation do so in such a manner that the greatest number of atoms (*i.e.*, giving the largest possible value for n) are in the closest possible approach to one another, thus allowing the maximum achievable intermolecular attractive force to become operative (where aromatic molecules are concerned this will mean practically that association will occur so that surfaces of greatest area are in contact).

Where the solute is non-polar by virtne of exact coaxial apposition of two strong dipoles well removed from each other, and the solvent has molecular dimensions roughly equal to those of the solute but differs in having only one large dipole, the following possibilities arise (illustrated by particular reference to *p*-dichlorobenzene in chlorobenzene solution). At considerable dilutions each *p*-dichlorobenzene molecule will be included between two aggregates of solvent molecules; it, together with its immediate neighbours, could be imagined as approaching either of the two extreme configurations shown sectionally as A_1 and A_2.



Obviously, the effect on the resultant moment of the solute will be different in the two cases. In A_2, equal but opposite induced moments will be set up in counteraction to the two permanent moments a and b: the net effect will therefore be zero. In this respect this configuration for the solvent molecules, among the infinitude possible between A_1 and A_2, is unique. In A_1, on the other hand, the effective moment indicated at a will be lowered whilst that at b will (at least) remain as before; the net resultant moment will therefore be finite.

The experimental results appear to indicate that the A_1 type of aggregation is favoured, *i.e.*, that the dipolar solvent units cluster around the solute with their dipoles in parallel rather than antiparallel alinement.

In this way the proportionality of the induced and the inducing dipoles is explained. It is interesting, therefore, to make an estimate of the polarisability, α, of the solute molecules on the basis of the model described in the diagram A_1. The expression $\mu_{\text{Induced}} = 2\alpha F$, where $F = (\mu/\varepsilon r^3)(\varepsilon + 2)/3$, should be applicable. In the case, *e.g.*, of *p*-dichlorobenzene in nitrobenzene, the experimentally measured value of μ_{Induced} is 1·65. If r (the distance between two molecules in A_1) be taken as *ca.* 3 Å., μ (the moment of nitrobenzene) as 4, and $(\varepsilon + 2)/\varepsilon$ be regarded as unity for large values of ε (ε_{PhNO_2} is *ca.* 35), we have $\alpha = 1$—2×10^{-23} e.s.u. Values of the same order are derivable for α from the results for the other solutions studied in this paper:

Solvent.	C_6H_6.	Ph·Ph.	*p*-$C_6H_4Cl_2$.	*pp'*-$C_6H_4Cl{\cdot}C_6H_4Cl$.
C_6H_5Cl	1·29	1·70	1·45	1·45
$C_6H_5{\cdot}NO_2$	1·37	1·70	1·49	1·81

Comparison with the experimental results of Stuart and Volkmann (*Z. Physik*, 1933, **80**, 107) is satisfactory. These authors, from measurements of the Kerr effect, give the polarisability of the benzene ring in its plane as $1{\cdot}23 \times 10^{-23}$, and the average polarisability of a benzene molecule as $1{\cdot}03 \times 10^{-23}$. In addition, it is noteworthy that the average polarisabilities (derived from the molecular refractivities $[R_L]_D$) of the molecules in question are: benzene, 1·03; diphenyl, 1·97; *p*-dichlorobenzene, 1·42; 4 : 4'-dichlorodiphenyl, 2·48. It is clear, therefore, that our results are reasonably explained by the physical picture to which allusion has been made. If the average polarisabilities are

divided into the three components in each case, it will be noticed that with benzene and its *p*-dichloro-derivative the agreement is good between our experimental α value and the calculated figure for the greatest axis of length, but with the diphenyl compounds the result found is too small. This may be due to the fact that the polarisable parts of the solute molecules are more remote from the polarising solvent units, or it may arise from a tendency for the solvent molecules to associate symmetrically in groups of four around a solute of the diphenyl type so that all induction effects are, in the resultant, cancelled out. The observed μ_{induced} for these compounds should therefore be smaller than would be the case if the simple arrangement assumed for the above calculations were to occur uniformly throughout the solutions.

Possible Alternative Explanations.—In the calculation of our results from the actual measurements of d and ε, etc., we have divided the observed total polarisations of the solutions into P_1f_1 and P_2f_2 by a simple mixture formula. This treatment when the solvent is non-polar—or practically so—is usually correct to the order of experimental accuracy. The solvent in such cases greatly preponderates, and its polarisation is independent of the concentration. The objection may be raised that this condition does not obtain in our experiments. To quote three examples: the values of P_2 for chlorobenzene, benzonitrile, and nitrobenzene as pure liquids are 61, 92, and 64 c.c., but as solutes at infinite dilution in the common non-polar solvents they are 80—85, 300—360, and 350—370 c.c. respectively; their polarisations (and those of all polar liquids of type A—see Le Fèvre and Le Fèvre, *loc. cit.*) are markedly affected by the dilution. In our measurements, while the concentration of the solute is becoming greater (*i.e.*, as f_1 is increasing) the solvent is becoming more dilute. Accordingly, its P_2 should be increasing, and our measured $P_1f_1 + P_2f_2$ might therefore contain the effect of this higher polarisation. Since from this (experimental) result we subtract P_2f_2 calculated on the basis of P_2 for the pure solvent (and this is liable to be for each solution erroneously small), P_1f_1—and hence P_1—may appear incorrectly large.

However, we are of the opinion that this effect is not present sufficiently to invalidate the conclusions previously stated. It will be noticed that P_1 shows throughout a tendency to rise as f_1 decreases. If P_2 were diminishing in the way described at the same time the reverse order for the P_1 figures would be expected. The apparent insensitiveness of P_1 to changes in f_1, however, may very likely be in some cases due to the superimposition of the (normal) P_{solute} increase and this (polar) solvent effect (decrease of P_2) with diminution of f_1.

The errors produced by inconstancy of P_2 should clearly become greater as f_2 diminishes; extrapolation, therefore, of P_1 (apparent) back to $f_1 = 0$ should furnish a value of $_{\infty}P_1$ free from uncertainties of the type under examination; in no case, however, has this process indicated a value approaching that appropriate for the substance in, *e.g.*, benzene solution.

A priori estimation of the significance of this effect in our solutions is difficult because either P_1 or P_2 has to be assumed constant (or at least its variation with concentration must be known) before the observed polarisation of the solution can be analysed into its component factors. Pal (*Phil. Mag.*, 1930, **10**, 265) and Sutton and Jenkins (J., 1935, 609) have studied the changes of polarisation of benzene–nitrobenzene mixtures with variation of f_1 and f_2, and have calculated the P_{PhNO_2} on the assumption of a fixed polarisation for benzene throughout—just the assumption the validity of which we are now led to question. If, *e.g.*, Pal's conclusions are used as a basis for correction of our results, it is observed that for dilute solutions of benzene in nitrobenzene, the P_{PhNO_2} is nearly linear with concentration. From a curve, "corrected" values of P_2 can be read off and used in the tables given later. In this way, the final P_1 is admittedly lowered in all cases where the method has been tried; the exaltation over the polarisation figure corresponding to $\mu = 0$, however, does not seem to be entirely eliminated even by this treatment.

Lastly, it might be urged, in criticism of our view, that in chloroform solution benzene appears to be practically non-polar, and that this solvent is one whose polarisation is almost the same whether measured in the liquid, dissolved, or gaseous state (Le Fèvre and Le Fèvre, *loc. cit.*), and is therefore one whose polarisation contribution should be

calculable accurately for all concentrations. Our difficulty here is that nothing *a priori* can certainly be said regarding the structure of the solutions; but, if a similar argument to that developed for the aromatic liquids may be used, we should not expect any marked change in the moment of the solute, an expectation which is in agreement with the experimental results.

EXPERIMENTAL.

Materials.—A commercial " pure " specimen of *p*-dichlorobenzene was recrystallised several times from alcohol; m. p. 52—53°. We are indebted to Dr. E. E. Turner for gifts of pure diphenyl and its 4 : 4′-dichloro-derivative. The various liquids were purified by usual methods, and when used as solvents, were always redistilled prior to use to remove traces of moisture which, when present, seriously disturb the dielectric-constant measurements. The b. p.'s were those recorded in the literature in all cases save that of *o*-dichlorobenzene : this boiled steadily over a small range (172—178°) and may therefore have contained some *p*-isomeride as an impurity. The density observed, however, is in good agreement with that given by Philip (J., 1912, **101**, 1868).

Method.—The dielectric constants and densities of the solutions at 25° were determined by the resonance method (J., 1935, 480), and the polarisations of the solutes calculated as indicated above.

The significant data for 25° are collected in the following tables, in which the symbols P and f refer respectively to the molecular polarisation and the molar fraction of the components in the solutions, the subscripts 1 and 2 applying to solute and solvent respectively; ε and d denote the dielectric constant and density of the solutions.

p-*Dichlorobenzene in benzene.*

$f_1 . 10^6$ ...	0	13297·0	14652·1	17856·0	33306·0
ε	2·2725	2·2756	2·2759	2·2767	2·2803
d	0·87368	0·88063	0·88127	0·88293	0·89090
$P_1f_1+P_2f_2$	26·5900	26·7361	26·7527	26·7889	26·9596
P_1	—	*37·58*	*37·69*	*37·73*	*37·69*

p-*Dichlorobenzene in carbon tetrachloride.*

$f_1 . 10^6$ ...	0	10699	14069·6	22696·2	394020
ε	2·2287	2·2319	2·2329	2·2354	2·2405
d	1·58454	1·58143	1·58045	1·57791	1·57299
$P_1f_1+P_2f_2$	28·2395	28·3335	28·3630	28·4383	28·5888
P_1	—	*37·02*	*37·02*	*37·00*	*37·10*

p-*Dichlorobenzene in dimethylaniline.*

$f_1 . 10^6$ ...	0	44001·0	51991·6	72904·1	90001·9
ε	4·8495	4·7558	4·7450	4·7007	4·6635
d	0·95198	0·96515	0·96746	0·97390	0·97918
$P_1f_1+P_2f_2$	71·4336	70·3563	70·2176	69·6923	69·2525
P_1	—	46·95	48·04	47·55	47·20

p-*Dichlorobenzene in chlorobenzene.*

$f_1 . 10^6$ ...	0	20014·7	29997·9	36663·5	52707·2
ε	5·6120	5·5463	5·5126	5·4894	5·4398
d	1·10085	1·10489	1·10687	1·10822	1·11140
$P_1f_1+P_2f_2$	61·9177	61·7184	61·6125	61·5351	61·3829
P_1	—	51·96	51·74	51·48	51·77

p-*Dichlorobenzene in ethyl benzoate.*

$f_1 . 10^6$	0	43998·2	58980·9	72903·0
ε	5·7658	5·6546	5·6151	5·5729
d	1·04446	1·05309	1·05580	1·05882
$P_1f_1+P_2f_2$	88·1351	86·5373	86·0009	85·4211
P_1	—	51·82	51·95	50·0

p-*Dichlorobenzene in* o-*dichlorobenzene.*

$f_1 . 10^6$	0	20012·0	31332·7	39245·2
ε	6·8281	6·7348	6·6835	6·6426
d	1·29381	1·29360	1·29347	1·29342
$P_1f_1+P_2f_2$	75·0077	74·6078	74·3847	74·2016
P_1	—	55·03	55·12	54·48

p-*Dichlorobenzene in benzonitrile.*

$f_1 . 10^6$ ...	0	52555·3	105778·6	120998·9
ε	25·200	23·822	22·561	22·111
d	1·00088	1·01734	1·03373	1·03841
$P_1f_1+P_2f_2$	91·5593	91·4907	91·4213	91·3376
P_1	—	90·25	90·26	89·73

p-*Dichlorobenzene in nitrobenzene.*

$f_1 . 10^6$	0	28201·0	43975·9	76563·1	95651·0
ε	34·890	33·501	32·723	31·182	30·239
d	1·19852	1·20122	1·20265	1·20553	1·20759
$P_1f_1+P_2f_2$	94·2807	94·2588	94·2397	94·1917	94·1017
P_1	—	93·50	93·35	93·12	92·41

Benzene in chloroform.

f_1	0	0·036524	0·057436	0·140865
ε	4·7240	4·5779	4·4919	4·1630
d	1·46814	1·44409	1·43029	1·37624
$P_1f_1+P_2f_2$	45·0799	44·4397	44·0437	42·3836
P_1	—	*27·55*	*27·04*	*25·04*

Benzene in chlorobenzene.

f_1	0	0·073737	0·106258	0·190284
ε	5·6120	5·3775	5·2780	5·0111
d	1·10085	1·08562	1·07929	1·06190
$P_1f_1+P_2f_2$	61·9177	60·0977	59·2780	57·0735
P_1	—	*37·24*	*37·07*	*36·46*

Benzene in nitrobenzene.

f_1	0	0·050997	0·057915	0·106981
ε	34·89	32·853	32·630	30·783
d	1·19861	1·18427	1·18232	1·16834
$P_1f_1+P_2f_2$	94·2736	93·1505	93·0072	91·9000
P_1	—	72·25	72·41	72·09

Diphenyl in benzene.

f_1	0	0·005201	0·008689	0·012111
ε	2·2725	2·2754	2·2774	2·2794
d	0·8738	0·87561	0·87670	0·87805
$P_1f_1+P_2f_2$	26·5850	26·7085	26·7922	26·8716
P_1	—	*50·33*	*50·43*	*50·25*

Diphenyl in chlorobenzene.

f_1	0	0·004019	0·010544	0·034602
ϵ	5·6120	5·5943	5·5642	5·4469
d	1·10085	1·10036	1·09975	1·09734
$P_1f_1+P_2f_2$	61·9177	61·9432	61·9650	62·0015
P_1	—	68·26	66·40	64·34

Diphenyl in nitrobenzene.

f_1	0	0·014801	0·033482	0·052476
ϵ	34·89	33·874	32·681	31·280
d	1·19861	1·19481	1·19025	1·18465
$P_1f_1+P_2f_2$	94·2736	94·6889	95·1971	95·7180
P_1	—	122·30	121·86	121·80

4 : 4′-Dichlorodiphenyl in benzene.

f_1	0	0·005208	0·011346	0·024588
ϵ	2·2725	2·2772	2·2826	2·2939
d	0·87380	0·87789	0·88271	0·89273
$P_1f_1+P_2f_2$	26·5850	26·7879	27·0225	27·5318
P_1	—	65·53	65·14	65·09

4 : 4′-Dichlorodiphenyl in chlorobenzene.

f_1	0	0·006127	0·006894	0·011645
ϵ	5·6120	5·5773	5·5735	5·5472
d	1·10085	1·10262	1·10283	1·10422
$P_1f_1+P_2f_2$	61·9177	62·0051	62·0193	62·0860
P_1	—	76·18	76·65	76·37

4 : 4′-Dichlorodiphenyl in nitrobenzene.

f_1	0	0·009777	0·015007	0·024373
ϵ	34·89	34·1693	33·7798	33·0900
d	1·19861	1·19966	1·20027	1·20129
$P_1f_1+P_2f_2$	94·2736	94·7722	95·0302	95·4915
P_1	—	145·27	144·69	144·24

Carbon disulphide in benzene.

f_1	0	0·021799	0·040002	0·074353	0·169211
ϵ	2·2725	2·2789	2·2842	2·2941	2·3194
d	0·8738	0·87901	0·88332	0·89158	0·91573
$P_1f_1+P_2f_2$	26·5850	26·5071	26·4420	26·3149	25·9055
P_1	—	23·01	23·01	22·95	22·57

Carbon disulphide in chlorobenzene.

f_1	0	0·121411	0·125168	0·172855
ϵ	5·6120	5·3596	5·3479	5·2478
d	1·10085	1·11180	1·11193	1·11641
$P_1f_1+P_2f_2$	61·9177	57·5792	57·4363	55·7468
P_1	—	26·18	26·12	26·22

Carbon disulphide in nitrobenzene.

f_1	0	0·108787	0·174559	0·183080
ϵ	34·89	32·191	30·507	30·278
d	1·19861	1·20081	1·20246	1·20274
$P_1f_1+P_2f_2$	94·2736	89·5589	86·6568	86·2722
P_1	—	50·94	50·64	50·57

The comparison between benzene and carbon disulphide seemed of particular interest from the point of view discussed above (p. 489). The molecular weights of these two solutes are very nearly identical, and if the polarisation effects now reported are ascribable to P_2 changes—rather than to induction in the solute molecules—then at the same concentrations in, *e.g.*, nitrobenzene these two substances should exhibit nearly the same apparent polarisations. Inspection of the tables shows that they do not do so, either in nitro- or in chloro-benzene solution.

SUMMARY.

(1) The typical non-polar substances named in the title become apparently polar when dissolved in polar solvents.

(2) The degree of apparent polarity so induced varies roughly directly with the moment of the solvent.

(3) These observations can be harmonised with a qualitative picture previously given.

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116. *Solvent Effect in Dipole-moment Measurements. The Polarisations of Chloro- and Nitro-benzene, Chloroform, and Bromoform in a Series of Polar Solvents.*

By R. J. W. LE FÈVRE and P. RUSSELL.

THE substances for which data have already been recorded (Le Fèvre and Le Fèvre, J., 1935, 1747) fall roughly into two classes, in one of which the total polarisation in the pure state is considerably less than, and in the other of which it is of the same order as, the total polarisation in the "infinitely dilute" (non-polar solvents) and/or the gaseous state. Molecules of compounds of these types were designated A and B respectively, and were distinguished by their Kerr constants. A very broad geometrical definition of the two groups was attempted, and a mechanism suggested whereby these factors could affect the observed polarisations.

The purpose of the present paper is to extend and illustrate the latter point by reference to two typical substances of each shape class, *viz.*, nitro- and chloro-benzene, both of type A (positive Kerr constants), and chloroform and bromoform, both of type B (negative Kerr constants).

Applicability of Existing Rules for Solvent Effects.—Several quantitative relations are extant connecting the polarisation of a solute with the dielectric constant of the medium and other factors (for references, see Goss, *Trans. Faraday Soc.*, 1934, **30**, 751; Frank, *Proc. Roy. Soc.*, 1935, **152**, 171). The majority are evidently of no general applicability for the reason implicitly stated before (Le Fèvre and Le Fèvre, *loc. cit.*), *viz.*, that the polarisations they forecast for substances in the vapour state are always higher than those in the liquid or dissolved condition (cf. *Trans. Faraday Soc.*, 1934, **30**, 860); *e.g.*, chloroform is a well-authenticated exception to this generalisation (*Nature*, 1935, **136**, 181), and certain amines behave in the same way. These rules considered only the *solvent*.

In certain other rules, *e.g.*, those of Weigle (*Helv. Physica Acta*, 1933, **6**, 68) and Frank (*loc. cit.*), (1) and (2) respectively,

$$\Delta\mu = A\mu^3 n(\alpha_1 - \alpha_2)^2/a^6kT + B\mu n(\alpha_1 + 2\alpha_2)/3 \quad . \quad . \quad . \quad . \quad (1)$$

$$\Delta\mu = (A_1 + A_2)\mu(\varepsilon - 1)/\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$_0P_{\text{liq.}} = {_0P_{\text{gas}}} + [(\varepsilon - 1)/(\varepsilon + 2)]N\Theta/3kT \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

both solute and solvent properties are recognised, but the possibility (Le Fèvre and Le Fèvre, previous paper) that "non-polar" substances (such as benzene and carbon disulphide) can acquire considerable moments by dissolution in polar solvents markedly narrows the validity range, in as much as μ, the true moment in the gaseous state, is for these compounds zero, whence $\Delta\mu$ also should vanish.

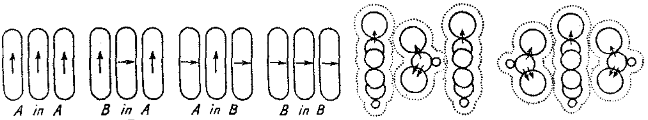
Equation (3) (see Le Fèvre and Le Fèvre, *loc. cit.*) for the orientation polarisation of a substance in a medium of dielectric constant ε should, it is true, apply—by its derivation —only to pure substances and not to solutions. Nevertheless, it is obvious that a similar expression might be correct, for Θ can have either sign (depending ultimately on the shape of the molecule) and includes effectively such molecular properties as the polarisabilities of the compound along the three axes. The difficulty of evaluating Θ from *a priori* data, however, seriously limits the practical application of this equation at present; some calculations of Θ from Le Fèvre and Le Fèvre's experimental data show, moreover, that it varies with the solvent. Used in the manner required if (3) is to be applied to solutions, it cannot have the significance $\Theta = \Sigma\mu_1^2 s_1 + 2\Sigma\mu_1\mu_2 q_{12}$ given to it by Raman and Krishnan. It must presumably contain two terms at least, referring severally to the solute and the solvent molecules. The necessity for this is seen by considering two solutions : A in A and A in B. If A and B have the same dielectric constants, then in going from one to the other Θ must change its sign and value with the change of solvent. Similarly, for the pair A in A and B in A, the same change must accompany the change of type of solute. It would appear, therefore, that no equation for the polarisation of a substance in solution has yet been satisfactorily established.

A Qualitative Treatment for the Solvent Effect.—The picture presented by Le Fèvre and Le Fèvre (*loc. cit.*) for the polarisation effects observed with *pure* liquids can be extended and utilised to predict correctly the results obtained when either polar or non-polar solutes are examined in polar or non-polar solvents. Those authors predicted that "a solvent of type A will be more effective in apparently reducing the orientation polarisation of a solute of its own type than in apparently increasing the corresponding polarisation of one of type B; again, a solvent of type B will cause smaller diminution of polarisation of an A type solute than it will an increase of polarisation of a solute of the second kind." The measurements now recorded were initiated to test this prediction. Their success justifies a more particular description than this quotation affords.

The tendency towards organised structures in liquids and solutions can be ascribed to forces of the van der Waals type operating between the molecules. The most stable structures will therefore be those in which the maximum number of atoms can make the closest possible approach; *i.e.*, where $E = \Sigma(-C/R^6)$ = a maximum — an expression for E, the mutual energy, of the type $E = -C/R^6 + be^{-R/S}$ being envisaged (cf. Born and Mayer, *Z. Physik*, 1932, **75**, 1; London, *Z. physikal. Chem.*, 1931, *B*, **11**, 222). The specifications of the molecular types A and B can be given, more accurately than was previously

done, as those in which the principle moment lies roughly respectively *in*, or *at* 90° *to*, the *plane of greatest polarisability*. The latter will, in general, be the plane of greatest area.

The following procedure can be used to forecast the polarisation changes consequent upon dissolution, etc., of a substance. Imagine the solvent molecules aggregated about the solute so that the maximum number of atoms are in contact, and then consider the induction effects due to the moments in the solvent molecules on the solute unit so enclosed. Where aromatic compounds are under consideration especially, but probably generally, only two molecules of solvent to one of solute need be taken. Four arrangements suggest themselves for discussion, represented schematically as sections in (I), (II), (III), and (IV).



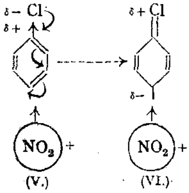
I II III IV IIa IIIa

Illustration of Method.—Chlorobenzene and nitrobenzene, either as pure liquids separately, or mutually dissolved, will conform to pattern (I). Because their polarisabilities are greatest along the length axis, considerable induction of moment in a reversed direction to the permanent resultant will be effected. A lowering of moment, and hence polarisation, will occur.

The induction will depend upon the polarisability of the solute, the moment of the solvent, and the distances between the molecules, etc. It is possible that in some cases the induced moment might outweigh the permanent moment; *e.g.*, *p*-dichlorobenzene in nitrobenzene acquires an induced moment of the order of that of chlorobenzene itself. In this connexion a calculation of the induced moment by the equation set out in the preceding paper is of interest. If R be taken as 3·5 Å. (Katz, *Z. angew. Chem.*, 1928, **41**, 329), μ as equal to the moments determined in the gaseous state, and α as the value derived from the molar refraction, then the orders of the induced moments are as in col. 5 :

Solute.	Solvent.	α_{solute}.	$\mu_{solvent}$.	$\mu_{induced}$.	$\mu_{gas}-\mu_{induced}$.
$PhNO_2$	$PhNO_2$	1·3	4·23	0·9	3·3
PhCl	PhCl	1·2	1·69	0·4	1·3
$PhNO_2$	PhCl	1·3	1·69	0·5	3·7
PhCl	$PhNO_2$	1·2	4·23	0·8	0·9

and the figures in col. 6 should correspond to the experimentally found values. These are 1·7, 1·2, 2·5, and 1·6, respectively, and, from their orders at least, afford some support to the views now advanced. The inversion of polarity of chlorobenzene by neighbouring polar nitrobenzene molecules is not without analogy to the electromeric polarisation generally assumed to occur prior to *p*-substitution when the essential part of a kationoid reagent approaches the *o*- or the *p*-nuclear position [cf. (V) and (VI)].



(V.) (VI.)

Chloro- and nitro-benzene dissolved in choroform are considered as in (III*a*), but owing to the tetrahedral dispositions of the C–Cl dipoles in the chloroform, they cannot, since induction varies as the cube of the distance, all three equally affect the most polarisable parts of the solute (*viz.*, the C–Cl or the $C-NO_2$ bond). For induction to lead to an *increase* of moment, the ratio between the distance of one C–Cl dipole of the chloroform molecule from the C–X of the solute to the (equal) distances of the other two C–Cl dipoles must be greater than $1/2^{\frac{1}{3}}$—the ratio for which neither increase nor decrease occurs. From the geometry of the chloroform molecule, it seems certain that the actual ratio must be smaller.

Nitro- and chloro-benzene should therefore show a slight reduction of moment in chloroform solution. The moments found are *ca.* 3·0 and 1·2 respectively. For analogous reasons, these solutes should show a reduction of polarisation in carbon disulphide, and, in fact, they do.

Solutions of chloroform and bromoform in chloro- and nitro-benzene can be considered on the basis of (II*a*). Here the dipoles of the solvents will (see above) reduce the nearest C–X dipole in the CHX_3 solute more than they will increase the other two. Since the resultant moments of chloroform and bromoform have the nature of a difference of three components, the net effect is to cause an increase. This is observed, particularly with nitrobenzene as solvent. It is of interest that the increases over the value in benzene (*viz.* 0·26 for chloro- and 0·38 for bromo-form) are in nearly the same ratio as the average polarisabilities of these molecules (*viz.*, 0·8 and 1·2 × 10^{-23} e.s.u.).

The effect of benzene as a solvent is to *raise* the polarisation of chloroform and lower those of chloro- and nitro-benzene compared with the gaseous values. This effect is most marked with the last solute. According to the qualitative picture described above, all three compounds should show higher moments in benzene solution (at infinite dilution) than in the vapour phase. This may really be the case, and pending further investigation we note that, for substances whose moments are between 1 and 4 as solutes, the weakest solution with which trustworthy observations can be made (say, *ca.* f_1 = 0·005) corresponds to a number of solnte molecules per c.c. roughly equal to that obtaining in the vapour of the substance at atmospheric pressure. For dipole-moment determinations in the gaseous state, the dielectric-constant estimations are generally made at pressures lower than this; hence, the minimum concentration for one method is roughly the maximum concentration for the other. In proportion, therefore, and in the same direction, as the P_1 is affected by mutual induction effects between the solute molecules, so will the estimated ${}^{\infty}P_1$ be correct, *i.e.*, the extrapolated polarisations for nitro- and chloro-benzene in solvents will always tend to be too low, whilst for chloroform, and generally for substances of the B shape class, the reverse should occur.

Results.—The measurements were made by methods set out before and are tabulated below under self-explanatory headings. The total polarisations at infinite dilution were calculated from the experimental figures, it being assumed that for dilute solutions both dielectric constant and density are linear functions of the concentration (Hedestrand, *Z. physikal. Chem.*, 1929, *B*, **2**, 428), *i.e.*, that $\varepsilon_{soln.} = \varepsilon_{solvent}(1 + \alpha f_1)$ and $d_{soln.} = d_{solvent}(1 + \beta f_1)$, f_1 being the mol.-fraction of the solute; then ${}^{\infty}P_1 = A(M_1 - B\beta) + C\alpha$, where $A = (\varepsilon_2 - 1)/(\varepsilon_2 + 2)d_2$, $B = M_2/d_2$, and $C = 3M_2/[(\varepsilon_2 + 2)^2 d_2]$.

The values obtained by graphical estimation are included (in parentheses) for comparison.

Solute.	Solvent.	Total P_1, c.c.	Orientn. poln., c.c.	Apparent μ.
C_6H_5Cl	(gas)			1·69
	(liquid)	62	31	1·22
$[R_L]_D$ = 31	C_6H_6	82·8 (82)	52 (51)	1·59 (1·57)
	$CHCl_3$	60·1 (61)	29 (30)	1·18 (1·20)
	$C_6H_5{\cdot}NO_2$	84·9 (84)	54 (53)	1·62 (1·60)
$C_6H_5{\cdot}NO_2$	(gas)			4·23
	(liquid)	94	61	1·72
$[R_L]_D$ = 33	C_6H_6	371·7 (347)	339 (314)	4·05 (3·90)
	$CHCl_3$	225·2 (218)	192 (185)	3·05 (2·99)
	C_6H_5Cl	161·3 (158)	128 (125)	2·49 (2·46)
$CHCl_3$	(gas)			1·06
	(liquid)	45	24	1·10
$[R_L]_D$ = 21	C_6H_6	52·1 (52)	31	1·22
	C_6H_5Me	52·6 (52)	32 (31)	1·24 (1·22)
	C_6H_5Cl	47·9 (48)	27	1·18
	$C_6H_5{\cdot}NO_2$	66·5 (67)	45·5 (46)	1·48 (1·49)
$CHBr_3$	(liquid)	47	17	0·91
	C_6H_6	52·9 (52)	23 (22)	1·06 (1·03)
$[R_L]_D$ = 30	$CHCl_3$	45·0 (46)	15 (16)	0·85 (0·88)
	C_6H_5Cl	47·1 (48)	17 (16)	0·91 (0·93)
	$C_6H_5{\cdot}NO_2$	72·7 (73)	43	1·44

Solvent constants used.

Solvent.	A.	B.	C.	Solvent.	A.	B.	C.
C_6H_6	0·3409	89·28	14·67	PhCl	0·5504	102·19	5·291
C_6H_5Me	0·3674	107·69	16·90	$Ph{\cdot}NO_2$	0·7665	102·62	0·2262
$CHCl_3$	0·3772	81·40	5·401				

Dielectric constant and density coefficients.

Solute.	Solvent.	α.	β.	Solute.	Solvent.	α.	β.
C_6H_5Cl	C_6H_6	3·566	0·2578	$C_6H_5{\cdot}NO_2$	C_6H_6	23·262	0·3782
,,	$CHCl_3$	0·6981	−0·4522	,,	$CHCl_3$	31·44	−0·2931
,,	$C_6H_5{\cdot}NO_2$	−38·616	−0·0941	,,	C_6H_5Cl	19·88	0·1024
$CHCl_3$	C_6H_6	1·894	0·5384	$CHBr_3$	C_6H_6	1·7532	1·9749
,,	C_6H_5Me	1·6363	0·4798	,,	$CHCl_3$	− 0·6851	1·5218
,,	C_6H_5Cl	− 0·5243	0·3020	,,	C_6H_5Cl	− 1·0236	1·5413
,,	$C_6H_5{\cdot}NO_2$	−28·38	0·2372	,,	$C_6H_5{\cdot}NO_2$	−37·99	1·4442

Materials.—The substances used in this and the following investigation were commercially pure specimens, purified by redistillation immediately before use in order to remove small traces of moisture which greatly diminish the sharpness of the resonance curve in the dielectric-constant determination.

All determinations relate to 25°.

Chlorobenzene in benzene.

$f_1 \cdot 10^6$	0	22973	57267	125128
ε	2·2725	2·3540	2·4790	2·7158
d	0·87370	0·87968	0·88848	0·90559
P_1	—	81·64	81·31	78·40

Chlorobenzene in chloroform.

$f_1 \cdot 10^6$	0	21182	37554	83665
ε	4·7240	4·7381	4·7509	4·7836
d	1·46814	1·45836	1·45125	1·43090
P_1	—	60·30	60·27	59·75

Chlorobenzene in nitrobenzene.

$f_1 \cdot 10^6$	0	35649	61809	106235
ε	34·89	33·490	32·539	30·796
d	1·19861	1·19526	1·19277	1·18865
P_1	—	84·38	84·47	83·72

Nitrobenzene in benzene.

$f_1 \cdot 10^6$	0	34216	69472	70239
ε	2·2725	3·0537	3·9011	3·9239
d	0·87370	0·88667	0·89993	0·90025
P_1	—	314·9	281·8	281·6

Nitrobenzene in chloroform.

$f_1 \cdot 10^6$	0	39602	62531	90352
ε	4·7240	5·9669	6·7001	7·5569
d	1·46814	1·45656	1·44979	1·44163
P_1	—	199·8	189·4	177·3

Nitrobenzene in chlorobenzene.

$f_1 \cdot 10^6$	0	46199	70873	80073
ε	5·6120	6·5149	7·0275	7·2258
d	1·10085	1·10560	1·10808	1·10904
P_1	—	154·4	151·1	149·9

Chloroform in benzene.

$f_1 \cdot 10^6$	0	65875	89280	147558	148847
ε	2·2725	2·3965	2·4406	2·5541	2·5557
d	0·87370	0·90894	0·92175	0·95336	0·95413
P_1	—	51·24	50·86	50·46	50·36

Chloroform in toluene.

$f_1 \cdot 10^6$	0	140614	166891	225595
ε	2·3721	2·5997	2·6438	2·7471
d	0·85429	0·92112	0·93414	0·96386
P_1	—	50·86	50·60	50·20

Chloroform in chlorobenzene.

$f_1 \cdot 10^6$	0	82172	96741	123919
ε	5·6120	5·5804	5·5588	5·5482
d	1·10085	1·11952	1·13006	1·13850
P_1	—	46·43	46·81	46·44

Chloroform in nitrobenzene.

$f_1 \cdot 10^6$	0	92818	148010	264948
ε	34·890	32·250	30·673	27·372
d	1·19861	1·22028	1·23386	1·26256
P_1	—	66·81	66·58	66·11

Bromoform in benzene.

$f_1 \cdot 10^6$	0	65880	116063
ε	2·2725	2·3881	2·4758
d	0·87370	1·00382	1·10290
P_1	—	51·24	50·73

Bromoform in chloroform.

$f_1 \cdot 10^6$	0	20525	45276	56328
ε	4·7240	4·7107	4·6926	4·6838
d	1·46814	1·49939	1·53698	1·55373
P_1	—	45·10	44·81	44·68

Bromoform in chlorobenzene.

$f_1 \cdot 10^6$	0	26522	121695	124844
ε	5·6120	5·5850	5·4890	5·4819
d	1·10085	1·14132	1·28926	1·29433
P_1	—	48·34	48·24	48·03

Bromoform in nitrobenzene.

$f_1 \cdot 10^6$	0	76036	150528	152577
ε	34·89	31·953	29·296	29·066
d	1·19861	1·30755	1·41776	1·41892
P_1	—	72·91	72·00	72·45

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117. *The Apparent Dipole Moment of Paraldehyde in Various Solvents.*

By R. J. W. Le Fèvre and P. Russell.

These measurements were started because paraldehyde was reported to have a large negative Kerr constant (*viz.*, − 713; cf. Wolf, *Leipzige Vorträge*, 1929, 129). Owing however, to the fact that even carefully purified paraldehyde, which had been several times frozen, etc., always gave positive aldehyde tests with dinitrophenylhydrazine, observations on this substance were excluded from the preceding paper. If the position of the equilibrium $(C_2H_4O)_3 \rightleftharpoons 3CH_3{\cdot}CHO$ is altered by solvents,* the interpretation of our results would be significantly affected, because, whereas the moment of paraldehyde is evidently of the order 2 D units, that of acetaldehyde is 2·7 or even higher.

Our numerical results are tabulated as in the previous paper.

Polarisations and apparent moments of paraldehyde in various solvents.

Solvent.	Total poln., c.c.	Orientn. poln., c.c.	Apparent μ.
(Paraldehyde)	106·6	73·5	1·89
Carbon tetrachloride	126·1 (125) *	93 (92)	2·12 (2·11)
Benzene	117·8 (122)	85 (89)	2·03 (2·08)
Chloroform	138·2 (139)	105 (106)	2·26 (2·27)
Dimethylaniline	91·4 (92)	58·5 (59)	1·68 (1·69)
Chlorobenzene	98·1 (98)	65	1·77
Ethyl benzoate	97·2 (97)	64	1·76
o-Dichlorobenzene	100·4 (98)	67 (65)	1·80 (1·77)
Benzonitrile	111·3 (111)	78	1·94
Nitrobenzene	112·8 (113)	80	1·97

* The significance of data in parentheses is explained in the preceding paper (p. 494).

Solvent constants used (supplementary to those recorded in the previous paper, except those for chlorobenzene).

Solvent.	A.	B.	C.	Solvent.	A.	B.	C.
CCl_4	0·1832	97·20	16·32	$Ph{\cdot}CO_2Et$	0·5876	143·61	7·144
$NPhMe_2$	0·5904	127·10	8·128	o-$C_6H_4Cl_2$	0·5102	113·42	4·337
PhCl	0·5503	102·17	5·290	Ph·CN	0·8886	102·87	0·4171

Dielectric-constant and density coefficients for solutions of paraldehyde in the following solvents.

Solvent.	α.	β.	Solvent.	α.	β.
CCl_4	5·36	−0·814	C_6H_5Cl	3·49	−0·124
C_6H_6	5·29	0·157	$Ph{\cdot}CO_2Et$	2·25	−0·0420
$CHCl_3$	12·30	−0·714	o-$C_6H_4Cl_2$	2·62	−0·335
$NPhMe_2$	2·05	0·0426	Ph·CN	−13·9	0·00160
$Ph{\cdot}NO_2$	−26·00	−0·222			

Paraldehyde.—This was a commercially pure specimen; after redistillation and freezing, it had b. p. 124°/760 mm., m. p. 10—12°, $d_{4°}^{25°}$ 0·98960, and $\epsilon_{25°}$ 12·934 (Walden, *Z. physikal. Chem.*, 1903, **46**, 176, gives $\epsilon_{20°}$ for a wave-length of 72 cm. as *ca.* 11·8). From these data the total polarisation is 106·6 c.c.

The data for solutions in various solvents at 25° follow.

In carbon tetrachloride.

$f_1 \cdot 10^6$	0	22385	56869	83079	123846
ϵ	2·2270	2·3457	2·5331	2·6733	2·8920
d	1·58440	1·56628	1·53745	1·51644	1·48515
P_1	—	123·60	122·94	121·09	118·49

In benzene.

$f_1 \cdot 10^6$	0	27225	39252	46045	61544
ϵ	2·2725	2·4159	2·4802	2·5079	2·6027
d	0·87370	0·87796	0·87988	0·88074	0·88334
P_1	—	115·98	115·62	114·47	110·09

* A calculation on the basis of Pauling's figures shows that the energy changes involved in the passage from the right to the left side of this equation are of the same order as those for the keto $\rightleftharpoons$ enol change, which, as K. H. Meyer has demonstrated, is sensitive to the solvent employed.

In chloroform.

$f_1 \cdot 10^6$	0	27472	49000	80923	142580
ϵ	4·7240	5·0617	5·3293	5·7204	6·4533
d	1·46814	1·44803	1·43258	1·41078	1·36987
P_1	—	136·92	135·80	133·42	129·42

In dimethylaniline.

$f_1 \cdot 10^6$	0	41355	49434	82316
ϵ	4·8495	4·9386	4·9489	5·0133
d	0·95198	0·95381	0·95403	0·95544
P_1	—	91·92	90·96	90·62

In chlorobenzene.

$f_1 \cdot 10^6$	0	37117	48490	76503	89248
ϵ	5·6120	5·7415	5·7836	5·8778	5·9219
d	1·10110	1·09655	1·09507	1·09157	1·08999
P_1	—	97·94	98·29	97·94	97·92

In ethyl benzoate.

$f_1 \cdot 10^6$	0	70508	135423
ϵ	5·7658	5·9256	6·0680
d	1·04446	1·04153	1·03872
P_1	—	96·82	96·28

In o-dichlorobenzene.

$f_1 \cdot 10^6$	0	62578	79098	91727
ϵ	6·857	6·997	7·062	7·096
d	1·29608	1·27846	1·26961	1·26544
P_1	—	98·37	98·09	98·13

In benzonitrile.

$f_1 \cdot 10^6$	0	43816	110430	140900
ϵ	25·200	24·630	23·625	23·172
d	1·00127	1·00193	1·00308	1·00361
P_1	—	110·29	109·26	108·99

In nitrobenzene.

$f_1 \cdot 10^6$	0	32364	38657	107852
ϵ	34·890	34·082	33·862	32·037
d	1·19861	1·19150	1·19000	1·17460
P_1	—	112·78	112·61	112·51

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118. *The Progressive Elimination of Bromine in the Aqueous Hydrolysis of Sodium Bromoacetate.*

By HARRY BROOKE and HARRY M. DAWSON.

THE hydrolysis of sodium bromoacetate is represented stoicheiometrically by equation (A),

$$CH_2Br{\cdot}CO_2Na + H_2O = CH_2(OH){\cdot}CO_2H + NaBr \quad . \quad . \quad . \quad (A)$$

but kinetic observations indicate that the actual mechanism by which the reaction products are formed involves a number of simultaneous processes some of which occur in stages.

The initial velocities for solutions of varying concentration (Dawson and Dyson, J., 1933, 49) show that the formation of bromide in neutral solution is the result of two independent processes in which the primary reactants are, respectively, the bromoacetate ion and the water molecule (reaction 1) and two bromoacetate ions (reaction 2). As the hydrolysis proceeds and the solution becomes increasingly acid, the actual rates of bromide formation at successive stages are much greater than those calculated on the assumption that the observed rate is determined by reactions (1) and (2). In the case of 1·0*M*-sodium bromoacetate, the actual rate at the stage represented by the liberation of 50% of the total bromine is approximately twice as great as the rate calculated on this basis.

There can be no doubt that the glycollic acid formed is in part responsible for the discrepancy, and an attempt has been made to ascertain the nature of the processes which collectively determine the actual rate of bromide formation. The results show clearly that a large number of processes are involved. Some of these are associated with complex intermediate compounds the formation of which makes it impossible to give a complete account of the mechanism. It has, however, been established with very considerable probability that there are four other bimolecular processes, involving directly or indirectly the original bromoacetate and the final product glycollic acid, which play an effective part in the elimination of bromine as bromide in the progressive hydrolysis of the bromoacetate.

Although glycollic is a weaker acid than bromoacetic the difference is not very great and the equilibrium (B) is without doubt a factor of the first importance in determining

$$CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2H \rightleftharpoons CH_2(OH){\cdot}CO_2' + CH_2Br{\cdot}CO_2H \quad . \quad . \quad (B)$$

the rate of formation of bromide in the acid solutions. The establishment of this equili-

brium is directly responsible for the incidence of three further processes previously described (cf. Dawson and Dyson, J., 1933, 1133), which lead to the formation of bromide. The reactants in these are, respectively, the bromoacetic acid and water molecules (reaction 3), the bromoacetic acid molecule and the bromoacetate ion (reaction 4), and the bromoacetate and glycollate ions (reaction 5). For these five primary processes, the characteristic velocity coefficients have already been determined at 25° under "standard" conditions, *i.e.*, with a total salt concentration of 1·0 mol. per litre, and it seemed possible that the actual velocities at successive stages in the hydrolysis of a given original solution of sodium bromoacetate would be accounted for on the basis of the corresponding five partial velocities, provided that complications arising from the formation of intermediate compounds are avoided. That this is not the case is clearly shown by measurements of the initial velocities for solutions of sodium bromoacetate to which glycollic acid has been added. For all such mixtures the observed initial velocity is appreciably greater than that represented by the sum of the velocities of reactions (1) to (5). This may be illustrated by the data for 0·5*M*-sodium bromoacetate + 0·5*M*-glycollic acid, in which case the observed initial velocity at 25° is $11·7 \times 10^{-6}$ mol./l./min., whilst the calculated velocity is $9·3 \times 10^{-6}$. It thus appears that some other collisional process (or processes) must play a part in the liberation of bromine.

For convenience of reference the established reactions (1) to (5) and the corresponding bimolecular velocity coefficients are shown in Table I, which includes a number of other possible bimolecular processes, which might be considered responsible for the above discrepancy between the observed and calculated rates of elimination of bromine in the acid solution which results from the hydrolysis of sodium bromoacetate.

TABLE I.

(1)	$CH_2Br{\cdot}CO_2' + H_2O$	$k_1 = 0·059 \times 10^{-6}$
(2)	$CH_2Br{\cdot}CO_2' + CH_2Br{\cdot}CO_2'$	$k_2 = 19·3 \times 10^{-6}$
(3)	$CH_2Br{\cdot}CO_2H + H_2O$	$k_3 = 0·041 \times 10^{-6}$
(4)	$CH_2Br{\cdot}CO_2H + CH_2Br{\cdot}CO_2'$	$k_4 = 72 \times 10^{-6}$
(5)	$CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2'$	$k_5 = 35 \times 10^{-6}$
(6)	$CH_2Br{\cdot}CO_2H + CH_2(OH){\cdot}CO_2'$	$k_6 = 136 \times 10^{-6}$
(7)	$CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2H$	$k_7 = (0)$
(8)	$CH_2Br{\cdot}CO_2H + CH_2(OH){\cdot}CO_2H$	$k_8 = (0)$
(9)	$CH_2Br{\cdot}CO_2H + CH_2Br{\cdot}CO_2H$	$k_9 = (0)$
(10)	$CH_2Br{\cdot}CO_2H + OH_3^{\cdot}$	$k_{10} = (0)$

With regard to the several bimolecular processes (6)—(10) it is to be noted that measurements of the reaction velocity for solutions of widely varying hydrogen-ion concentration afford no evidence for the elimination of bromine by the interaction of the bromoacetic acid molecule with the hydrogen ion (10), or by the interaction of pairs of bromoacetic acid molecules (9). Since the latter process is ineffective under the experimental conditions used, as is implied by the symbol (0), it seemed unlikely that collisions of the bromoacetic acid molecule with the glycollic acid molecule (8), or, indeed, with any other un-ionised acid molecule would lead to the liberation of bromide, and the ineffectiveness of such collisional processes is shown by the results obtained with mixtures of bromoacetic acid and other weak acids under conditions in which the acids are practically un-ionised.

Previous experiments (Dawson and Dyson, *loc. cit.*) with bromoacetic acid in presence of nitric acid have shown that the rate of formation of bromide is accurately represented in terms of reaction (3), and it has now been established that the rate of formation remains sensibly unchanged in the presence of glycollic acid. The same result is obtained when other acids are substituted for the glycollic acid. Table II gives the initial velocities in mols./l./min. at 25° for these mixed acids in presence of 0·5*M*-nitric acid and 1·0*M*-sodium nitrate to provide as far as possible the "standard" conditions which characterise these experiments so far as salt content is concerned. It is probable that the nitric acid, which is added to prevent ionisation of the weak acids, has itself an inert-salt effect, but this is small and has been neglected. In this and subsequent tables the velocity v represents the actual velocity $\times 10^6$.

TABLE II.

Initial velocities for mixtures of bromoacetic and other un-ionised acids; 25°.

	v.
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H$	0·110
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}1M$-$CH_2(OH){\cdot}CO_2H$	0·1095
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}2M$-$CH_2(OH){\cdot}CO_2H$	0·109
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}3M$-$CH_2(OH){\cdot}CO_2H$	0·1085
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}1M$-$CH_3{\cdot}CO_2H$	0·109
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}2M$-$CH_3{\cdot}CO_2H$	0·1075
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}2M$-$C_2H_4(CO_2H)_2$	0·106

The slight fall observed in the presence of the second acid is probably due to the small change in the reaction medium, and the obvious conclusion from these results is that bromide ion is not liberated with appreciable velocity by the interaction of the bromoacetic acid molecule with the molecules of other carboxylic acids. This result is in line with the ineffectiveness of the collisions between pairs of bromoacetic acid molecules (9).

For all the solutions in Table II, the observed velocity would therefore seem to be attributable to the action of water on the bromoacetic acid molecule. In view of the inactivity of the un-ionised weak acids it might be suggested that reaction (3) is somewhat anomalous, but this is probably not the case, for if the concentration of the water were of the same order as that of the acids in Table II ($<$ 1 mol. per litre) the velocity due to (3) would scarcely be measurable. The effectiveness of this reaction under the conditions of these experiments is thus attributable to the very large concentration of the solvent molecules. Similar considerations apply to reaction (1), in which bromide ion is eliminated from the bromoacetate ion by the action of the water molecule.

With regard to reactions (6) and (7), it is to be noted that the two sets of reactants are the reversible pairs involved in the equilibrium (B), and since the concentration products of the two pairs have a fixed ratio, it is evident that the differentiation between (6) and (7) as the cause of bromide formation is attended by peculiar difficulties. The effectiveness of one (or both) of these reactions has, however, been established with certainty by measurements of the initial velocities for solutions represented stoicheiometrically by

$$aM\text{-}CH_2Br{\cdot}CO_2Na + bM\text{-}CH_2(OH){\cdot}CO_2H.$$

Provided that the ratio b/a in these solutions is not greater than *ca.* 10 the equilibrium (B) takes the form

$$(a-x)CH_2Br{\cdot}CO_2' + (b-x)CH_2(OH){\cdot}CO_2H \rightleftharpoons xCH_2(OH){\cdot}CO_2' + xCH_2Br{\cdot}CO_2H$$

for which the constant K is given by

$$K = K_g/K_b = x^2/(a-x)(b-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)$$

in which K_g and K_b are the ionisation constants of glycollic acid and bromoacetic acid respectively in the "standard" solution. From equation (C), x may be derived, and the sum of the velocities of reactions (1)—(5) is then given by

$$v_{calc.} = k_1w(a-x) + k_2(a-x)^2 + k_3wx + k_4x(a-x) + k_5x(a-x) \quad . \quad (D)$$

If the difference between $v_{obs.}$ and $v_{calc.}$ is denoted by v_r and attributed to reactions (6) and (7) then

$$v_r = v_6 + v_7 = k_6x^2 + k_7(a-x)(b-x) \quad . \quad . \quad . \quad . \quad . \quad (E)$$

whence

$$v_r/x^2 = k_6 + k_7/K = \text{const.}$$

The initial velocities obtained for mixtures of sodium bromoacetate and glycollic acid agree closely with the above deduction, as may be seen from Table III, in which the values of a and b are shown in cols. 1 and 2. Col. 3 gives the values of x derived from $K = K_g/K_b =$ 0·125, where $K_g = 2{\cdot}6 \times 10^{-4}$ and $K_b = 2{\cdot}05 \times 10^{-3}$ are the ionisation constants for glycollic and bromoacetic acid in $1M$-sodium nitrate solution. The ratio of these ionisation constants for the "standard" salt solution is practically identical with the ratio for pure aqueous solutions of the acids. Col. 4 gives the observed initial velocities (mols./l./min.),

and col. 5 records the velocities calculated from equation (D) by using the velocity coefficients recorded in Table I and $w = 54$. Col. 6 shows the difference v_r between the observed and calculated velocities, and col. 7 gives the values of v_r/x^2.

TABLE III.

Initial reaction velocities for aM-$CH_2Br{\cdot}CO_2Na + bM$-$CH_2(OH){\cdot}CO_2H$.

a.	b.	x.	$v_{obs.}$.	$v_{calc.}$.	v_r.	v_r/x^2.	a.	b.	x.	$v_{obs.}$.	$v_{calc.}$.	v_r.	v_r/x^2.
0·05	0	0	0·206	0·208	—	—	0·10	0	0	0·516	0·513	—	—
0·05	0·20	0·0239	0·297	0·217	0·080	140	0·10	0·20	0·0362	0·787	0·610	0·177	135
0·05	0·30	0·0276	0·313	0·209	0·104	136	0·10	0·30	0·0429	0·843	0·602	0·241	131
0·05	0·40	0·0302	0·323	0·201	0·122	134	0·10	0·40	0·0479	0·888	0·591	0·297	130
0·05	0·50	0·0322	0·334	0·195	0·139	134	0·10	0·50	0·0519	0·923	0·580	0·343	128

From the table it is clear that the differences between the observed velocities and those calculated on the basis of reactions (1)—(5) are very considerable and increase in each series with the concentration of the glycollic acid. At the same time, the approximate constancy of v_r/x^2 affords strong support for the view that the differences are due to the formation of bromide by either reaction (6) or reaction (7) or possibly by both. The fact that the values of v_r/x^2 tend to fall slightly with increasing glycollic acid concentration is possibly due to the gradually changing character of the reaction medium, which probably slightly affects all the velocity coefficients.

In order to obtain further evidence in support of the results which are summarised in the above table, similar experiments have been made with corresponding series of solutions in which the glycollic acid is replaced by acetic acid. The results are presented in Table IV, the form of which is identical with that of Table III. For this series of solutions the values of x are derived from $K = K_a/K_b = 0{\cdot}0132$ where $K_a = 2{\cdot}7 \times 10^{-5}$ is the ionisation constant of acetic acid in $1M$-sodium nitrate solution. The velocities are calculated from equation (D) with the substitution of $k_5 = 50 \times 10^{-6}$ for the reaction represented by $CH_2Br{\cdot}CO_2' + CH_3{\cdot}CO_2'$ which takes the place of reaction (5) of Table I in the glycollic acid series.

TABLE IV.

Initial reaction velocities for aM-$CH_2Br{\cdot}CO_2Na + bM$-$CH_3{\cdot}CO_2H$ (25°).

a.	b.	x.	$v_{obs.}$.	$v_{calc.}$.	v_r.	v_r/x^2.	a.	b.	x.	$v_{obs.}$.	$v_{calc.}$.	v_r.	v_r/x^2.
0·05	0	0	0·206	0·208	—	—	0·10	0·2	0·0145	0·640	0·593	0·047	225
0·05	0·2	0·0100	0·251	0·230	0·021	210	0·10	0·3	0·0175	0·674	0·611	0·063	205
0·05	0·3	0·0120	0·263	0·232	0·031	215	0·10	0·5	0·0221	0·728	0·620	0·108	220
0·05	0·4	0·0137	0·270	0·233	0·037	200	0·20	0	0	1·39	1·41	—	—
0·05	0·5	0·0150	0·280	0·233	0·047	210	0·20	0·4	0·0289	1·965	1·78	0·185	220
0·10	0	0	0·516	0·513	—	—	0·20	0·5	0·0321	2·05	1·81	0·24	230

The relations shown by Table IV are evidently quite similar to those in Table III and thus support the conclusion that bromide is formed by reaction (6) or (7) when glycollic acid is added to a bromoacetate solution. The kinetic data *per se* do not, however, permit of a distinction between (6) and (7) as the cause of the reaction velocity represented by v_r. On the other hand, since the liberation of bromide ion is very probably associated with the formation of an intermediate complex (cf. p. 503), reaction (6) would represent the simpler mechanism, in that (7) would seem to involve the simultaneous transfer of proton from one molecule to another.

Definite evidence in favour of (6) seems to be provided by experiments in which the bromoacetic acid in (6) has been replaced by ethyl bromoacetate, and the glycollic acid in (7) by ethyl glycollate. In these circumstances there is no complication due to the acid–base equilibrium, and the experiments show that bromide is readily liberated in the interaction of ethyl bromoacetate and the glycollate ion, but that no change takes place which can be attributed to the interaction of the bromoacetate ion with ethyl glycollate. It thus appears probable that v_r is attributable to the mechanism represented by (6). If this be accepted, the data in Table III lead to $k_6 = 136 \times 10^{-6}$, and the corresponding coefficient for the interaction between the bromoacetic acid molecule and the acetate ion (Table IV) is approximately 220×10^{-6}.

Idealised Hydrolysis of Sodium Bromoacetate.—Having thus obtained evidence of a sixth reaction which gives rise to bromide in acid solutions containing bromoacetate and glycollate, it will now be showu that the rate of elimination of bromine as bromide in solutions which correspond with successive idealised stages in the hydrolysis of sodium bromoacetate can be interpreted very satisfactorily in terms of the six reactions (1)—(6). In accordance with the established facts, it is assumed that reactions (7)—(10) are of negligible significance under the conditions of the experiments to be described.

The experimental data represent the initial velocities for synthetic solutions which contain the final reaction products in quantities such as would result from actual hydrolysis in the absence of intermediate compound formation. The only difference is that the synthetic solutions contain sodium nitrate instead of sodium bromide. It should be clearly recognised that these " idealised " solutions contain no complexes and therefore are not identical with those which are produced at the same stage (measured by the silver titration) in the progressive hydrolytic change. These " idealised " solutions correspond stoicheiometrically with the formula $aM\text{-}CH_2Br{\cdot}CO_2Na + bM\text{-}CH_2(OH){\cdot}CO_2H + (1 - a)M\text{-}NaNO_3$, in which $(a + b)$ is constant throughout the series. The value of x corresponding with equilibrium (B) is derived in the manner previously described, and in terms of a and x the total velocity due to reactions (1)—(6) is then given by

$$v_{calc.} = k_1w(a - x) + k_2(a - x)^2 + k_3wx + k_4x(a - x) + k_5x(a - x) + k_6x^2 \quad . \quad (F)$$

The results obtained for two such series of solutions with $a + b = 0{\cdot}5$ and $1{\cdot}0$ severally are shown in Table V. The first two columns give the values of a and x; the next six give the partial velocities attributable to reactions (1)—(6), and the sum of these ($v_{calc.}$) is shown in the penultimate column. The observed initial velocities for the various solutions are recorded in the last column.

TABLE V.

Velocity of bromide formation at successive idealised stages of the hydrolysis of sodium bromoacetate. Standard conditions and 25°.

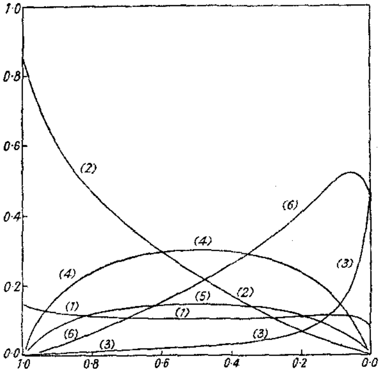
a.	x.	v_1.	v_2.	v_3.	v_4.	v_5.	v_6.	$v_{calc.}$.	$v_{obs.}$.
			Idealised stages for 0·5M-*sodium bromoacetate.*						
0·50	0	1·60	4·83	—	—	—	—	6·43	6·30
0·45	0·031	1·34	3·37	0·07	0·935	0·455	0·13	6·30	6·25
0·40	0·048	1·13	2·40	0·11	1·21	0·59	0·31	5·75	5·77
0·35	0·058	0·935	1·65	0·13	1·21	0·59	0·45	4·97	5·00
0·30	0·064	0·755	1·08	0·14	1·09	0·525	0·55	4·14	4·14
0·25	0·065	0·59	0·655	0·14	0·86	0·42	0·57	3·24	3·24
0·20	0·064	0·435	0·355	0·14	0·625	0·30	0·55	2·41	2·39
0·15	0·058	0·295	0·165	0·13	0·38	0·185	0·45	1·61	1·58
0·10	0·048	0·165	0·052	0·11	0·18	0·088	0·31	0·905	0·90
0·05	0·031	0·061	0·007	0·068	0·043	0·022	0·13	0·33	0·33
			Idealised stages for 1·0M-*sodium bromoacetate.*						
1·0	0	3·20	19·3	—	—	—	—	22·5	22·35
0·95	0·0375	2·92	16·10	0·08	2·47	1·20	0·19	22·95	23·2
0·90	0·0625	2·68	13·55	0·14	3·78	1·84	0·53	22·5	22·9
0·80	0·096	2·25	9·57	0·21	4·86	2·36	1·24	20·5	21·0
0·70	0·116	1·87	6·58	0·26	4·87	2·37	1·83	17·8	18·3
0·60	0·127	1·51	4·32	0·28	4·32	2·10	2·17	14·7	15·0
0·50	0·131	1·18	2·63	0·29	3·48	1·69	2·32	11·6	11·7
0·40	0·127	0·87	1·45	0·28	2·50	1·21	2·17	8·5	8·60
0·30	0·116	0·59	0·66	0·26	1·53	0·75	1·83	5·6	5·50
0·20	0·096	0·33	0·21	0·21	0·72	0·35	1·24	3·05	2·98
0·10	0·0625	0·12	0·03	0·14	0·17	0·08	0·53	1·07	0·99

For the first series the observed and the calculated velocities are in remarkably close agreement, and although the deviations are somewhat greater in the second series, it may justifiably be claimed that the observations give strong support to the view that reactions (1)—(6) are the only ones which play an effective part in the formation of bromide in so far as the intervention of intermediate complex compounds does not call for consideration.

In reference to the trend of the individual partial velocities, it may be noted that v_1

and v_2 diminish continuously as the " idealised " hydrolysis proceeds, but that the others pass through maximum values. For v_3 and v_6, which are proportional to x and x^2 respectively, the maxima are reached at 50% hydrolysis, whilst for v_4 and v_5, which are both proportional to $x(a - x)$, it may be shown that the maximum values correspond with 25% reaction. Further, it is noteworthy that the calculated total velocity for the 1·0M-solution passes through a maximum at about 5% hydrolysis, the decrease in v_1 and v_2 being more than counterbalanced by the increase in velocity attributable to v_3, v_4, v_5, and v_6. The maximum thus indicated by theory is entirely in accord with the experimental data, which show quite definitely that $v_{obs.}$ passes through a maximum value at about this stage of the reaction.

The relative importance of reactions (1)—(6) in the case of 1M-sodium bromoacetate at successive stages is shown in the figure. The curves show the respective fractions of the total velocity which are attributable to the several component reactions at each stage. It is noteworthy that the curve for (1) is for the most part a horizontal line, which signifies



Idealised hydrolysis of 1·0*M-sodium bromoacetate. Curves* (1)—(6) *represent the fractions of the total velocity which are attributable to the several component reactions at successive stages of the hydrolysis. The abscissæ give the molar concentration of the undecomposed bromoacetate.*

that the contribution of reaction (1) to the total velocity is represented by a nearly constant fraction (*ca.* 0·10) except at the beginning and the end of the change. This possibly affords an explanation of the fact that the actual course of the progressive hydrolysis of sodium bromoacetate conforms approximately to the requirements of the simple unimolecular formula (cf. Table VI). The fraction due to (2) falls rapidly and continuously from a high initial value, whilst the curve for (3) rises continuously and with increasing rapidity as the reaction progresses.

Reactions (4) and (5) are represented by curves of cycloidal type with maximum relative contributions at about 50% reaction, whilst the relative importance of (6) rises continuously until reaction has progressed to about 95%, where a maximum is reached.

When more than 90% of the total bromide ion has been liberated, the precise form of the curves cannot, however, be derived without taking into account the hydrogen-ion concentration of the solution.

The Progressive Hydrolysis of Sodium Bromoacetate.—Although the above experiments with idealised synthetic solutions serve to throw considerable light on the mechanism of this kinetically complex reaction, it must be recognised that the sequence of events in the ordinary progressive hydrolysis of sodium bromoacetate is further complicated by the circum-

stance that the formation of glycollic acid does not keep pace with the formation of bromide. This was attributed by Senter and Ward (J., 1912, **101**, 2534) to the formation of bromoacetoxyacetate, although the corresponding effect in the hydrolysis of sodium monobromosuccinate was supposed by Holmberg (*Ber.*, 1912, **45**, 1713) to be due to the intermediate formation of a lactone. The sum total of the facts now established affords no support for the latter hypothesis, but is quite consistent with the former. Having regard to the constitution of the acid solutions formed in the progressive hydrolysis of sodium bromoacetate, it thus seems probable that the retarded development of acidity is due to the formation of intermediate complexes which, for the reactions (2), (4), (5), and (6) are represented, respectively, by the formulæ

$$CH_2Br{\cdot}CO_2' + CH_2Br{\cdot}CO_2' \longrightarrow CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2' + Br' \quad . \quad . \quad . \quad (2)$$

$$CH_2Br{\cdot}CO_2' + CH_2Br{\cdot}CO_2H \longrightarrow CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2H + Br' \quad . \quad . \quad (4)$$

$$CH_2(OH){\cdot}CO_2' + CH_2Br{\cdot}CO_2' \longrightarrow CH_2(OH){\cdot}CO_2{\cdot}CH_2{\cdot}CO_2' + Br' \quad . \quad . \quad (5)$$

$$CH_2(OH){\cdot}CO_2' + CH_2Br{\cdot}CO_2H \longrightarrow CH_2(OH){\cdot}CO_2{\cdot}CH_2{\cdot}CO_2H + Br' \quad . \quad (6)$$

The rates of formation of these complexes are given by the partial velocities corresponding with v_2, v_4, v_5, and v_6, and the total concentration is measured at each stage of the hydrolysis by the difference between the silver and the alkali titration data if no complexes of higher order are formed. The rates of hydrolysis of the complexes are unknown and the individual concentrations (c_2, c_4, c_5, and c_6) cannot be estimated, but it is apparent that the ratios c_2/c_4 and c_5/c_6 must be controlled by the hydrogen-ion concentration of the solution, and further, that the ratio between the total bromoacetoxyacetate ($c_2 + c_4$) and the total glycolloxyacetate ($c_5 + c_6$) must vary as the reaction progresses. Since the anions of any weak organic acid may take the place of the glycollate ion in reactions (5) and (6), it seems probable that first-order complexes of the type $R{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2'$ may be directly responsible for the production of bromide by interaction with the bromoacetic ion or molecule to form second-order complexes of the type $R{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2'$. Such considerations lead to the conclusion that the course of progressive hydrolysis must be appreciably influenced by factors which have been eliminated in the experiments of Table V.

When the hydrolysis of the sodium bromoacetate has reached the stage corresponding with the elimination of 50% of the total bromine, the silver and the alkali titration data for the 1·0*M*-solution indicate that the total concentration of the intermediate complexes is approximately 0·1 mol. per litre. From the slope of the curve connecting the bromide concentration with the time, it is found that the actual rate of bromide formation at this stage in the progressive hydrolysis is $11{\cdot}5 \times 10^{-6}$ mol./l./min. For the idealised reaction the observed rate at the same stage has very nearly the same value, *viz.*, $11{\cdot}7 \times 10^{-6}$ (cf. Table V), although the synthetic solution contains considerably more bromoacetate and glycollic acid than the corresponding solution in the progressive hydrolysis. It thus seems impossible to avoid the conclusion that the intermediate complexes contribute directly to the rate of bromide formation and are not merely responsible for retarding the liberation of glycollic acid.

Having regard to the complexity of the mechanism of the progressive hydrolysis which is thus indicated, it is of interest to recall that Senter's observations on sodium chloroacetate at 102° (J., 1907, **91**, 460) indicate that the rate of hydrolysis, as measured by titration with alkali, is approximately proportional to the chloroacetate concentration until the reaction is more than half complete. In view of this apparent simplicity, the actual course of the reaction for 1·0 and 0·5*M*-solutions of sodium bromoacetate, as measured by both silver and alkali titration, has been examined under "standard" conditions with reference to the unimolecular formula $k' = (1/t)\log_e c_0/c$. The data recorded in Table VI represent the times required for the reaction to proceed 10, 20, 30 . . .% towards completion as measured by silver titration on the one hand, and by alkali titration on the other; these numbers are derived from the large-scale graphs which incorporate the extensive series of actual measurements. The values of k' for the two series of titrations are distinguished by k_{Br} and k_{Ac}.

TABLE VI.

Progressive hydrolysis of 1·0M-*sodium bromoacetate* (25°).

[Bromide], mols./l.	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8
$t\,.\,10^{-3}$ (mins.)	4·6	9·3	14·6	21·5	29·7	39·8	55·7	82·2
$10^6\,.\,k_{Br'}$	22·9	24·0	24·4	23·8	23·3	23·0	21·6	19·6
[Acid], mols./l.	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8
$t\,.\,10^{-3}$ (mins.)	7·5	13·6	20·7	29·5	40·8	55·2	73·9	106·5
$10^6\,.\,k_{Ac'}$	14·1	16·4	17·2	17·3	17·0	16·6	16·3	15·1
[Bromide], mols./l.		0·05	0·1	0·15	0·2	0·25	0·3	0·35
$t\,.\,10^{-3}$ (mins.)		8·3	16·8	26·5	37·8	51·4	69·3	95·0
$10^6\,.\,k_{Br'}$		12·7	13·3	13·5	13·5	13·5	13·2	12·7
[Acid], mols./l.		0·05	0·1	0·15	0·2	0·25	0·3	0·35
$t\,.\,10^{-3}$ (mins.)		11·7	22·0	34·3	48·7	66·4	88·5	121·5
$10^6\,.\,k_{Ac'}$		9·0	10·1	10·4	10·5	10·4	10·2	9·9

The data in the foregoing table show that the course of the reaction, whether followed by titration with silver or with alkali, can be expressed with fair approximation over a considerable range by the unimolecular formula. The mean values of $k_{Br'}$ and $k_{Ac'}$ show, however, large variations when the concentration of the bromoacetate is increased from 0·5 to 1·0. Having regard to the results previously described, it is apparent that the approximate applicability of the unimolecular formula is devoid of any real significance so far as the real mechanism of the reaction is concerned. The true value of the unimolecular velocity coefficient for the reaction between the bromoacetate ion and the water molecule (reaction 1) is $k_1w = 3{\cdot}2 \times 10^{-6}$ mol./l./min., which of course is quite independent of the concentration. There is no obvious connexion between this and the empirical values of $k_{Br'}$ which are recorded in Table VI.

SUMMARY.

The rate of elimination of bromine as bromide ion in the hydrolysis of sodium bromoacetate is increased in the later stages by effects which are attributable to the glycollic acid formed. The acid itself is not directly responsible for the observed increase in the reaction rate, but the glycollate ion, which is present in accordance with the equilibrium

$$CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2H \rightleftharpoons CH_2Br{\cdot}CO_2H + CH_2(OH){\cdot}CO_2',$$

gives rise to bromide by interaction with the bromoacetate ion and also with the bromoacetic acid molecule. The latter reaction plays a very important part in the liberation of bromide ion in the latest stages of the hydrolysis of sodium bromoacetate.

When effects arising from the formation of complex intermediate compounds are eliminated by the use of synthetic solutions which correspond with idealised stages of the reaction, it is found that the rate of liberation of bromide at all stages of the hydrolysis of sodium bromoacetate can be quantitatively expressed in terms of the velocities of six independent bimolecular processes in which the bromoacetate ion (or the bromoacetic acid molecule) reacts with the bromoacetate ion, the glycollate ion, or the water molecule.

The complexes formed in the actual progressive hydrolysis of sodium bromoacetate are not merely responsible for retarding the formation of glycollic acid, but are found to contribute appreciably to the rate at which bromide ion is eliminated from the bromoacetate.

Although the course of progressive hydrolysis under the usual conditions can be represented approximately by a unimolecular formula over a considerable part of the complete reaction, it is shown that this is an accidental circumstance which is without significance for the mechanism of this highly complicated reaction.

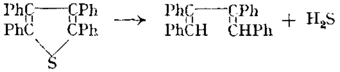
The authors are indebted to Imperial Chemical Industries Ltd. for a grant.

THE UNIVERSITY, LEEDS. [*Received, February 27th, 1936.*]

NOTES.

Reduction Experiments with 2 : 3 : 4 : 5-Tetraphenylthiophen. By ERNST BERGMANN.

A COMPOUND, m. p. 255°, stated without proof to be αβγδ-tetraphenylbutane, was obtained by Baumann and Klett (*Ber.*, 1891, **24**, 3307) by heating stilbene with sulphur and by Fromm and Achert (*Ber.*, 1903, **36**, 539) by the thermal decomposition of dibenzyl sulphide or dibenzyl disulphide or by the reduction of 2 : 3 : 4 : 5-tetraphenylthiophen with zinc and hydrochloric acid. The present author has described (*Annalen*, 1933, **500**, 122) an αβγδ-tetraphenylbutane, m. p. 86°. Although two diastereoisomeric forms are theoretically possible, the difference of the m. p.'s seems to be too great. On repetition, no tetraphenylbutane was obtained under the conditions of reduction reported by Fromm and Achert; only on treatment with sodium and amyl alcohol was the tetraphenylthiophen desulphurated and hydrogenated, αβγδ-tetraphenylbutane, m. p. 86°, and 1 : 2-diphenyl-3-benzylhydrindene, m. p. 182°, being formed. Both these substances have been obtained (*Annalen*, *loc. cit.*) by the same treatment of αβγδ-tetraphenyl-$\Delta^{\alpha\gamma}$-butadiene. Therefore the conclusion is obvious that the first step in the reduction of tetraphenylthiophen is the conversion into αβγδ-tetraphenylbutadiene :



Tetraphenylthiophen (18 g.) was prepared according to Baumann and Klett (*loc. cit.*) from stilbene (30 g.) and sulphur (9 g.) at 240° (6 hours), no higher-melting product being formed. After recrystallisation from amyl alcohol, the product had m. p. 178°. A portion (5 g.) was treated with zinc dust (30 g.) and concentrated hydrochloric acid (50 c.c.) in a boiling mixture of benzene (100 c.c.) and alcohol (40 c.c.) for 4 hours. After cooling, the solid was collected and extracted with boiling benzene, and pure tetraphenylthiophen (m. p. 185°) precipitated with alcohol. Reduction did not occur, even under more drastic conditions.

Reduction. Sodium (7 g.) was introduced in small portions into a boiling solution of tetraphenylthiophen (1·9 g.) in amyl alcohol (100 c.c.), the solution poured into 50% acetic acid, and the 1 : 2-diphenyl-3-benzylhydrindene collected and recrystallised from amyl alcohol; m. p. and mixed m. p. 181—182°. The filtrate was treated with steam, the residue dissolved in ether and dried, the solvent evaporated, and the αβγδ-tetraphenylbutane crystallised by trituration with light petroleum; m. p. and mixed m. p. 86°.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, December 9th, 1935.*]

Glucosides of the Glyoxaline Series. By E. BERGMANN and H. HEIMHOLD.

GULLAND and MACRAE (J., 1933, 663) prepared the glucoside of 4-methylglyoxaline from the silver derivative of the latter and tetra-acetobromoglucose. In the same way we have prepared (see Thesis, H. Heimhold, Berlin, 1932) from glyoxaline the crystalline *tetra-acetoglucosido-* and *triacetorhamnosido-glyoxaline* and have deacetylated them in the ordinary way. Tetra-acetogalactosido- and hepta-acetolactosido-glyoxaline were obtained only as syrupy masses. Our substances, too, showed a high resistance against acid hydrolysis, but it has been proved again that they do not contain free imino-groups.

Silver Glyoxaline.—To 14·2 g. of glyoxaline (b. p. 138°/14 mm.; Fargher and Pyman, J., 1919, **115**, 228) in 100 c.c. of water, 39 g. of silver nitrate, dissolved in 120 c.c. of water, and then 78 c.c. of 25% aqueous ammonia, were added. The white precipitate was washed with water, alcohol, and ether and dried. Yield, 31 g. (Found : Ag, 61·4. Calc. for $C_3H_3N_2Ag$: Ag, 61·7%).

N-*Glucosidoglyoxaline.*—The speed of the reaction between silver glyoxaline and acetohalogenoses depends largely on the surface properties of the silver compound. The reaction times given below are the maximal ones; sometimes the reaction finished in a quarter of the time stated.

Silver glyoxaline (2 g.) was heated for 4 hours with tetra-acetobromoglucose (4·1 g.) in 40 c.c. of xylene. *Tetra-acetoglucosidoglyoxaline* (1·5 g.) crystallised from the filtered solution on cooling. Recrystallisation from propyl alcohol gave silky needles, m. p. 205—208° (Found : C, 51·7; H, 5·7; N, 6·3. $C_{17}H_{22}O_9N_2$ requires C, 51·3; H, 5·5; N, 7·0%). 6·05 Mg. gave no

methane in the Zerewitinoff apparatus. According to the method of Zemplén and Pacsu (*Ber.*, 1929, **62**, 1613), 0·5 g. of the above compound in 5 c.c. of methyl alcohol was boiled with 2 c.c. of $N/10$-sodium methoxide for 8 minutes and left at 0° over-night; 0·14 g. of *glucosidoglyoxaline* separated as clusters of stout crystals, m. p. 217° after recrystallisation from propyl alcohol. The same compound was obtained when 3 g. of the above acetyl compound in 240 c.c. of methyl alcohol were saturated with gaseous ammonia and left at 0° over-night; after evaporation in a vacuum, the residue was recrystallised from a small amount of 50% alcohol, forming needles (0·5 g.), m. p. 217—218° (Found: C, 46·7; H, 6·3; N, 12·2; active H, 1·4, 1·5. $C_9H_{14}O_5N_2$ requires C, 47·0; H, 6·1; N, 12·2; active H, 1·7%). In 24% sulphuric acid (l = 1, c = 2·056%), α_D = 0·062°; $[\alpha]_D$ + 3·02°.

N-*Rhamnosidoglyoxaline.*—Silver glyoxaline (0·5 g.) and triacetobromorhamnose (1 g.) (Fischer, M. Bergmann, and Rabe, *Ber.*, 1920, **53**, 2371) were heated in 25 c.c. of xylene for 15 minutes; the solution was filtered into 200 c.c. of pure dry light petroleum; the small prismatic crystals of *triacetorhamnosidoglyoxaline* which separated were recrystallised from benzene; m. p. 177—179° (yield, 0·15 g.) (Found: N, 8·3. $C_{15}H_{20}O_7N_2$ requires N, 8·2%).

0·5 G. of the acetyl compound in 13 c.c. of methyl alcohol was heated for 5 minutes with 20 drops of $N/10$-sodium methoxide and kept over-night; the solvent was then evaporated in a vacuum, and the remaining syrup triturated with light petroleum. Recrystallisation from ethyl propionate gave clusters of prismatic needles, m. p. 153—156° (Found: C, 50·5; H, 6·3. $C_9H_{14}O_4N_2$ requires C, 50·5; H, 6·5%).

The experiments were partly carried out at the Friedrich Wilhelm University, Berlin; the Zerewitinoff determinations were made by Dr. Furter, Zurich.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, December 9th*, 1935.]

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s.-*Di*-p-*anisylpinacol.* By CHARLES W. SHOPPEE.

DI-*p*-ANISYL ketone 2 : 4-*dinitrophenylhydrazone*, orange-red laminæ, from ethyl acetate-ethyl alcohol, m. p. 197° (Found: C, 59·7; H, 4·4. $C_{21}H_{18}O_6N_4$ requires C, 59·7; H, 4·3%), was stirred in warm alcoholic suspension with aluminium foil (etched with $2N$-sodium hydroxide and amalgamated with ethereal mercuric chloride solution) for 3 hours (compare Cohen, *Rec. trav. chim.*, 1919, **38**, 75), the solution filtered after 12 hours, the residue repeatedly extracted with boiling alcohol, and the combined extracts and filtrate diluted with an equal volume of water. *s.-Di-p-anisylpinacol*, collected after 24 hours and crystallised from much hot alcohol (yield, 20%), formed colourless prisms, m. p. 183° (decomp.), giving a deep blue colour with concentrated sulphuric acid (Found: C, 74·3; H, 6·2. Calc. for $C_{30}H_{30}O_6$: C, 74·1; H, 6·2%). The final filtrate when largely diluted gave 4 : 4′-dimethoxybenzhydrol, m. p. 71° (compare Schnackenburg and Scholl, *Ber.*, 1903, **36**, 654).

Examination of the cooled melt, m. p. 115°, of the pinacol yielded only dianisyl ketone, m. p. 143° (Found: C, 74·35; H, 5·9. Calc. for $C_{15}H_{14}O_3$: C, 74·5; H, 5·8%), and 4 : 4′-dimethoxybenzhydrol, mixed m. p. 71°. An equimolecular mixture of these two substances has m. p. 115·5°. The pinacolin was not detected.

Attempts to prepare the pinacol by Bouvet's method (*Bull. Soc. chim.*, 1915, **17**, 209; he gives no experimental details) from anisylmagnesium bromide (4 mols.) and ethyl oxalate produced an oil consisting essentially of the substituted glycollic ester, $(p\text{-OMe}\cdot C_6H_4)_2C(OH)\cdot CO_2Et$. Migita's failure (*Bull. Chem. Soc. Japan*, 1932, **7**, 334) to obtain the pinacol by Gomberg and Bachmann's method (*J. Amer. Chem. Soc.*, 1927, **49**, 236) has been confirmed.

Anisyltrianisylmethyl Ketone.—The pinacol (0·5 g.) was refluxed with glacial acetic acid (5 c.c.) and a trace of iodine for ½ hour, and the cooled solution diluted. The precipitate, twice crystallised from alcohol, formed colourless prisms, m. p. 142°, giving a blue colour with concentrated sulphuric acid (Found: C, 76·8; H, 6·15. Calc. for $C_{30}H_{28}O_5$: C, 76·9; H, 6·0%). The ketone could not be obtained from dianisyl ketone by reduction with glacial acetic acid and zinc dust as stated by Migita (*loc. cit.*). Neither a semicarbazone nor a 2 : 4-dinitrophenylhydrazone could be prepared.

Anisoyldianisylcarbinol.—A solution of anisil (9 g.) in benzene–ether or anisole–ether was added to a Grignard reagent, prepared from magnesium (3·2 g.) and *p*-bromoanisole (25 g.), at 0°. After eventual heating on the steam-bath, the product was decomposed with ice, acidified with $2N$-sulphuric acid, and extracted with ether. The oil obtained by evaporation crystallised when rubbed with a little methyl alcohol; recrystallisation from ether–ligroin (b. p.

40—60°) and subsequently from methyl alcohol gave *anisoyldianisylcarbinol* in colourless rhombs, m. p. 117·5° (Found : C, 73·3; H, 5·9; OMe, 25·8. $C_{23}H_{22}O_6$ requires C, 73·0; H, 5·9; OMe, 24·6%).—THE UNIVERSITY, LEEDS. [*Received, March* 20*th*, 1936.]

1-*Methylbenzthiazole.* By J. FRASER and F. M. HAMER.

SINCE its first preparation (Hofmann, *Ber.*, 1880, **13**, 21) 1-methylbenzthiazole has been described in the literature as a liquid. In preparing several kilograms of it by Müller's method of treating 2 : 2′-dinitrodiphenyl disulphide with zinc dust, acetic acid, and acetic anhydride (*Z. Farbenind.*, 1906, **5**, 357), we collected the main fraction at 150—151° (uncorr.)/50 mm. On storage in a cold room, it solidified to colourless tabular crystals, m. p. 14°, which were of rectangular outline and showed straight extinction nnder the microscope.—KODAK LTD., WEALDSTONE, MIDDLESEX. [*Received, March* 10*th*, 1936.]

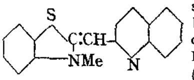
Reactivity of the Imino-group in 1-*Imino*-2-*methylbenzthiazoline.* By LESLIE M. CLARK.

SOME reactions of 2-methylbenzthiazoline (Mills, Clark, and Aeschlimann, J., 1923, **123**, 2353) and of its 1-nitrosoimino-derivative (Besthorn, *Ber.*, 1910, **43**, 1523) have already been recorded. Condensations involving the imino-group of 1-imino-2-methylbenzthiazoline (Besthorn, *loc. cit.*) are now described.

Reaction with Aniline.—This compound (1·6 g.) was boiled with aniline (1·4 g.) for 3½ hours, ammonia being evolved. The oily product crystallised in contact with a little alcohol, and recrystallisation from this solvent (charcoal) gave colourless plates, m. p. 95·5°, of 1-*phenylimino*-2-*methylbenzthiazoline* (Found : C, 69·6; H, 5·0; N, 11·5. $C_{14}H_{12}N_2S$ requires C, 70·0; H, 5·0; N, 11·7%).

Reaction with Phenylthiourea.—The thiourea and the imine in equimolecular proportion were heated at 220° for 4 hours, ammonia being evolved. The product crystallised from alcohol (charcoal) as a mixture of yellow prisms and pale yellow needles. Separation was readily effected, since the needles were considerably less soluble, and the prisms more soluble, in acetone than in alcohol. The prisms, m. p. 184°, were 1-*phenylthiocarbamylimino*-2-*methylbenzthiazoline* (Found : C, 60·2; H, 4·6; N, 13·7; S, 21·4. $C_{15}H_{13}N_3S_2$ requires C, 60·2; H, 4·35; N, 14·0; S, 21·35%). The needles, m. p. 261°, have not been identified (Found : C, 54·9; H, 3·9; N, 14·7; S, 25·8. $C_{17}H_{16}N_4S_2$ requires C, 54·8; H, 4·3; N, 15·0; S, 25·8%).

Reaction with Quinaldine.—1-Imino-2-methylbenzthiazoline (4 g.) was heated with quinaldine (4 g.) at 210° for 8 hours, ammonia being evolved. Volatile base was removed with steam, and addition of hydrochloric acid and alcohol to the dark residue gave a deep reddish-brown solution, from which an impure red monohydrochloride of 2-methylthio-ψ-cyanine crystallised. This was collected and warmed with concentrated hydrochloric acid, giving an almost colourless solution of the dihydrochloride—behaviour typical of the di-acid bases of the cyanine series. The solution was filtered from the comparatively insoluble imino-hydrochloride and basified. Crystallisation from alcohol and ethyl acetate gave 2-*methylthio*-ψ-*cyanine* (annexed formula) in yellow needles, m. p. 165° (Found : C, 74·1; H, 5·2; N, 9·5; S, 11·1. $C_{18}H_{14}N_2S$ requires C, 74·45; H, 4·9; N, 9·7; S, 11·05). The colourless acid solution gave with platinic chloride a pale buff-coloured *platinichloride* (Found : Pt, 27·9. $C_{18}H_{14}N_2S,H_2PtCl_6$ requires Pt, 27·9%.)



No reaction was observed between 1-imino-2-methylbenzthiazoline and α-picoline, acetoacetic ester, or malonic ester at the boiling point, and the evolution of ammonia when the imino-compound was heated with methyl-α- or -β-naphthathiazole at 240° was so slow that the reaction could not be used for synthesising intermediates in the thiocyanine dye series.

When thiourea or phenylthiourea was heated in boiling quinaldine solution, ammonia was evolved, but nothing crystalline was isolated.—WALNUT LANE, HARTFORD, CHESHIRE. [*Received, February* 15*th*, 1936.]

Radioactivity and Atomic Theory.

SIXTEENTH FARADAY LECTURE, DELIVERED AT THE ROYAL INSTITUTION ON FEBRUARY 12TH, 1936.

By LORD RUTHERFORD, O.M., D.Sc., LL.D., F.R.S.

NEARLY forty years have passed since the spontaneous radioactivity of uranium was shown by Becquerel in 1896. We know that the investigations which led to this fundamental discovery were much influenced by the discovery of *X*-rays by Röntgen in the preceding year. We can now look back with some sense of perspective and recognise the extraordinary importance of the discovery of radioactivity and the profound influence on our knowledge of atoms and the relation of the elements which has followed from a detailed study of the radioactive bodies.

In the course of this lecture, I have thought it of interest to give a brief account of some of the earlier experiments in radioactivity which pointed the way to the conclusion that the radioactive bodies were undergoing spontaneous transformation. This will be followed by a statement of the most significant of the discoveries that have resulted from an examination of the chemical and radioactive properties of the radio-elements. But this in a sense is only the beginning of the story. The use of swift α-particles to bombard matter gave us the first proof that certain light elements could be transformed by artificial methods. This has been followed in recent years by experiments in which streams of other fast particles, like protons, neutrons, and deuterons, have been artificially generated in order to bombard matter. By these methods, we have been enabled to extend widely our knowledge of the modes of transformation of the elements. In some cases, the nuclei of the atoms can be caused to break up with explosive violence, giving rise to new stable elements. In other cases, new radioactive bodies are produced which correspond to unstable isotopes of the elements. More than 50 of these artificially produced radioactive bodies are now known, and no doubt many more will be found in the near future.

The subject of radioactivity has indeed been born anew and has entered again on a new and vigorous phase of life. It is of interest to note that the methods developed long ago for the investigation of the radioactive bodies proper are now every day being applied to study the artificial transformation of elements and to follow the chemical changes involved. I have personally followed with great interest this ever-widening extension of the province of radioactivity, which to-day embraces so many workers and has already given us a new science in which the reactions occurring in the minute nucleus of an atom can be studied. The opening up of this new territory has only been made possible by the development of new and powerful electric methods of producing intense streams of bombarding particles with high speeds, and by the improvement of the automatic methods of counting swift particles and by the wide use of that wonderful instrument, the Wilson expansion chamber, to obtain visual evidence of the process of transformation.

Before discussing the changes in our ideas due to the study of radioactive transformations, we may pause for a moment to consider the prevailing ideas on atoms and their structure just before the discovery of radioactivity (1896), and the proof of the independent existence of the electron (1897). The atomic theory of Dalton had been almost universally accepted as the basis of the interpretation of the facts of chemistry. The work of the chemist for nearly a century had resolved our material world into 80 or more distinct types of atoms or elements, and had shown that the atoms of the elements were stable entities unchangeable by the chemical and physical forces then at our disposal. With increase of knowledge, the old ideas of the alchemists of the transmutation of the elements had been discarded, although it was recognised that one of the main problems of chemistry was to disclose the true relation of the elements and if possible to devise more potent methods capable of changing one element into another. This was well expressed by Faraday, " to decompose the metals, then, to reform them, to change them from one to another, and to realize the once absurd notion of transmutation, are the problems now given to the chemist for solution." To the philosophic mind, the periodic law of Mendeléef was of great signific-

ance in indicating that the atoms of the elements were not separate creations but closely related in their ultimate structure, but there was at that time no clue to the underlying meaning of this remarkable relation. It should be recalled that the periodic classification had been successful in predicting the properties of missing elements, and indeed, the position of several elements discovered later, after Moseley's generalisation, had been indicated correctly.

While the law of combining proportions did not involve any definite knowledge of the size and structure of atoms, yet the size and weight of the individual atoms had been roughly estimated from data based on the kinetic theory of gases. There was, however, little definite information to form any idea of the structure of atoms, although theoretical physicists like Larmor and Lorentz, in order to account for the vibrating properties of the atom as shown by its line spectrum, had suggested that the atom must consist of charged particles, but there was no evidence of the nature of the particles concerned. This difficulty, as we now know, was in part resolved by the discovery of the electron and the interpretation of the Zeeman effect. At this stage, although the relative atomic weights of many of the elements had been accurately measured, the ideas of atoms were very vague and uncertain. Although an enormous amount of information on the combining properties of atoms had been collected, and simple and useful working rules had been applied in explanation, more definite ideas of the underlying meaning of chemical combination had to await a much clearer conception of the electronic structure of atoms.

Early Experiments in Radioactivity.

My introduction to the subject of radioactivity began in a natural way in the Cavendish Laboratory, Cambridge, in 1897 as the result of earlier experiments on the ionisation produced in gases by *X*-rays. Becquerel had shown that the radiation from uranium caused the discharge of an electroscope, but had concluded that the radiation was different from *X*-rays in showing some evidences of refraction and polarisation. I proceeded to examine whether the ionisation was of the same type as that produced by *X*-rays and in the course of the work found that the rays were of two types, one easily absorbed, called the α-rays, and a more penetrating type, named the β-rays. A few observations were also made on the rays from thorium, which Schmidt in 1898 had found to be radioactive. Soon after my appointment to McGill University, Montreal, in 1898, Professor R. B. Owens and I began some experiments on the radiations from thorium, using the electrical method. We found that the effects produced by some thorium compounds, and particularly the oxide, appeared to be very capricious and much influenced by slight draughts of air in the testing vessel. Strong ionising effects were observed when thoria was covered with several sheets of paper, but only weak effects when the preparation was completely covered over by a thin sheet of mica. This peculiar inconsistency of the effects from thorium was at first very puzzling, as under the same conditions the radioactivity shown by uranium was quite constant.

In order to investigate the matter further, I arranged to pass a current of air over the thoria down a long tube and to examine the conductivity of the air in a large ionisation chamber by means of an electrometer. I then found that, on stopping the current of air, the ionisation effect fell off according to a geometrical law with the time, diminishing to half-value in about 1 minute. It thus seemed clear that thoria emitted some kind of active substance which was carried away with the air stream and decayed in activity with time. I gave the name " Emanation " to this unknown substance which readily diffused through paper.* This was the first time that the characteristic law of decay of radioactive bodies had been measured. At the same time, I noticed that all substances which came in contact with the emanation for some time became radioactive. This " excited " activity, as it was unfortunately termed, decayed with time after the removal of the emanation, according to the same law as the emanation but with a much longer half period, *viz.*, 4 hours instead of one minute. Another surprising result was observed in a strong electric field. The activity was to a large extent concentrated on the negative electrode. In this way, a platinum wire could be made strongly active. The activity on the wire could be driven off by heat and removed by solution in acids, but when the acid was evaporated, the

activity remained behind. These results were a strong indication that the activity was due to some kind of matter produced either from the emanation or by its action. It seemed likely that the emanation existed in very minute quantity, but it occurred to me that diffusion methods might throw light on whether the emanation was a light or a heavy substance. For this purpose, the relatively long-lived emanation from radium was employed. By measuring the coefficient of diffusion of the emanation into air, Miss H. T. Brooks and I concluded that its molecular weight was large and of the order of 100.

About this time, 1901, began that fruitful association with F. Soddy, who was then a teacher in the Chemical Department of McGill University. At this stage, the subject of radioactivity was in a very confused state. A number of substances had been found to show a temporary activity when separated from a radioactive solution or exposed to radioactive bodies, and the idea had arisen that the radiations had in some way the property of "inducing" radioactivity on bodies exposed to the radiation. This was a natural but mistaken idea which had to be cleared away before progress could be made. For this purpose we first made experiments on the thorium emanation to determine its chemical properties and to find whether it originated from thorium itself or from some other substance associated with it. We found that a new radioactive substance, named thorium-*X*, could be chemically separated from thorium and that this substance and not thorium itself gave rise to the emanation. It was found that thorium-*X* was being produced at a constant rate in the thorium and was converted into emanation. The constant activity due to thorium-*X* was shown to be the result of an equilibrium process in which the decay of the active matter was balanced by its continuous production. This process of production and decay was found to be a universal property of the radioactive bodies.

A study of the chemical properties showed that the emanation of both thorium and radium must be chemically inert and correspond to the group of gases of the helium–argon family. We now know that the radioactive emanations are isotopic representatives of the last of the inert gases. Finally, the material nature of the emanations was definitely established by proving they could be condensed in a spiral surrounded by liquid air. It is a noteworthy example of the delicacy and certainty of the methods of detection of radioactive matter that the chemical nature of the emanations and their condensation at low temperatures could be definitely established with almost infinitesimal amounts of active matter, far too small to be seen or weighed or detected by the spectroscope.

The experiments with thorium-*X* and the emanation gave ns for the first time a clear idea of radioactive processes and led us to put forward in 1902—1903 the transformation theory of radioactive elements. Although the results were substantiated and extended by investigations with other radioactive substances, time does not allow me to refer to them, and I must pass on at once to consider the importance of these new ideas on transformation.

The Transformation of Radio-elements.

The proofs that radioactivity was a sign and measure of the instability of atoms and that the radio-elements were undergoing spontaneous transmutation were contributions to our knowledge of outstanding importance. The long series of radioactive changes in uranium, thorium, and actinium were with few exceptions made clear during the next few years. There were thus brought to light more than 30 radio-elements, each of which showed distinctive radioactive behaviour and broke up according to a simple and definite law. In most cases, in the process of transformation, the radio-element emitted either a swift α-particle, now known to be a charged atom of helium, or a fast β-particle (negative electron). The transformation process is distinguished from an ordinary chemical reaction, not only because the disintegration appears to be spontaneous and unalterable by the forces at our command, but, most important of all, by the enormous amount of energy emitted from each exploding atom. This energy is for the most part emitted in the kinetic form of a swift α- or β-particle, but in some cases a part of the energy is emitted in the form of electromagnetic radiation of high frequency (γ-rays). Since there was a large emission of energy in the change of one atom into another, it was natural to infer that a large store of energy was contained in a heavy atom. It was clear, too, that the atom must be the seat of

intense internal forces in order to be able to hurl out a fragment of itself with such high speed.

Since experiments are usually made with small quantities of active matter or with elements like radium of slow rate of transformation, it is not easy to realise except in imagination the extraordinary effects that would be observed if we could, for example, experiment with a reasonable quantity of a short-lived element like the gas radon. Suppose we were able to obtain a kilogram of this gas and introduce it into a bomb made of heat-resisting material. At the end of about 2 hours, heat would be evolved corresponding to about 20,000 kilowatts and the bomb would be melted unless it were very efficiently cooled. Penetrating γ-rays would be emitted with energy corresponding to about 1,000 kilowatts. The heating effect would die away with the decay of radon (half period 3·8 days). At the end of about 2 months the radon would mostly have disappeared, but in its place would remain about 54 grams of the gas helium, and deposited on the walls 946 grams of a lead isotope (radium-*D*, atomic weight 210), mixed with a small quantity of radium-*E* and polonium. After allowing about 200 years for most of the radium-*D* to disappear, we should then find remaining about 72 grams of helium and 928 grams of an inactive lead isotope of atomic weight 206. I cannot imagine a more convincing experiment to illustrate the striking nature of these radioactive transformations, but unfortunately, or rather fortunately having regard to the safety of the investigator from the radiations, there is little chance of trying such a large-scale experiment.

The property of radioactivity, apart from uranium and thorium and their products, is shown only by a few other elements, potassium, rubidium—to which may now be added samarium—and then only to a very feeble degree. All the rest of the chemical elements appear to be permanently stable when tested by the criterion of radioactivity.

When once the nature of the α- and β-particles had been established and the long series of radioactive changes in uranium, thorium, and actinium had been mostly made clear, it appeared that the main contribution of radioactivity to our knowledge was nearing an end. But it is characteristic of this subject that no sooner does it appear to be visibly moribund than it flashes out again into vigorous life, leading to new and unexpected additions to our knowledge. This is well illustrated by the work of the next few years, 1911—1913, which saw three new advances of great significance for the future—I refer to the idea of the nuclear structure of atoms, the conception of the isotopic constitution of the elements, and the proof of an extraordinarily simple relation between the chemical properties of the radio-elements known under the name of the " Displacement Law."

The discovery of the electron in 1897 and the proof that it was a constituent of all atoms gave a great impetus to the belief that atoms were electrical structures. In 1904, Sir J. J. Thomson had proposed his well-known model atom and devised methods for estimating the number of electrons contained in each atom. On account of its mass and great energy of motion, the α-particle offered great advantages as a projectile to investigate the inner structure of atoms. It was known that it travelled through matter in nearly a straight line and must penetrate freely the structure of the atoms in its path. In addition, the scintillation method provided a delicate means of counting individual α-particles. The proof that the α-particle occasionally suffered a deflection through a large angle as the result of a single collision provided clear evidence that enormous deflecting forces existed within the atom. From these observations, I was led in 1911 to the idea that the atom was a very open electronic structure containing at its centre a very minute charged nucleus in which most of the mass of the atom was concentrated. The properties of the atom were defined by an integer representing the number of units of resultant charge carried by the nucleus. The fine experiments of Geiger and Marsden gave convincing evidence of the accuracy of the laws of scattering of α-particles calculated on this hypothesis and also gave us approximate estimates of the nuclear charge of the elements. As you know, this conception that the properties of the atom are defined by an integral number was verified and extended by the splendid experiments of Moseley on the *X*-ray spectra of the elements. He showed that the properties of an atom depended on its ordinal number, and identified this with the nuclear charge—a result later substantiated by Chadwick by direct determination of the nuclear charge by scattering experiments. Moseley's work was of far-reaching importance,

for it fixed once for all the number of the elements between hydrogen and uranium and gave the atomic number and X-ray spectra of the missing elements, several of which have since been discovered.

The next two important discoveries were a direct consequence of a very careful study of the chemical properties of the radio-elements. Several observers had noted that it was impossible chemically to separate certain radioactive elements when mixed together, for example, thorium and ionium, radium-D and lead, radium and mesothorium, although these elements showed quite distinctive radioactive properties and were believed to be of different atomic weights. Soddy concluded that these elements of identical chemical properties must occupy the same place in the periodic table, and gave them the name of "isotopes." This was the first time that proof had been obtained that an element might be complex and consist of atoms differing in mass and strncture. The complexity of the radio-elements is now well established. The three well-known radioactive series contain, for example, 6 isotopes of thorium, 3 of radium, 7 of lead, and 7 of polonium, and each of these isotopes shows a different mass and distinctive radioactive behaviour.

The next notable advance was the proof that the position of a radio-element in the periodic table had a very simple connexion with the type of radiation emitted by the parent product. Soddy had early noted several cases in which the emission of an α-particle, which carries two units of positive charge, gave rise to a product which had the chemical properties of an element two places preceding its parent in the periodic table. We now know that the effect of an emission of a β-particle, which carries only one unit of negative charge, is a corresponding displacement of one group in the opposite direction. The more complete generalisation had to await a more definite knowledge of the chemical nature of some of the products, much of which was supplied by the careful work of Fleck. The essential features of this process, known as the displacement law, were put forward about the same time in 1913 by Fajans, by A. S. Russell, and by Soddy, and not only included within their scope nearly all the radioactive bodies in the three main families, but even predicted the properties and positions of elements hitherto unobserved. The proof of this relation indicated that the periodic grouping of the elements was closely connected with the loss or gain of charge of the atom due to the expulsion of an α- or β-particle.

While the displacement law, as put forward, is quite independent of any special theory of the atom, yet we see that it is in complete accord witb the nuclear theory if we suppose that the α- and the β-particle are released from the nucleus. The atomic number and atomic weights of uranium and thorium being known, the atomic number and weight of each of the successive elements can be written down from a knowledge of the radiations emitted by each element—illustrating the extraordinary simplicity of the laws which hold for atomic nuclei.

The new conception of the isotopic constitution of the radio-elements naturally had a great influence in promoting experiments to decide whether the ordinary inactive elements also were complex. Very largely owing to the pioneer work of Aston, the broad features of the isotopic constitution of the great majority of the elements were soon established, indicating that the varieties of stable atoms were much more numerous than had been supposed.

Artificial Transmutation.

We now come to a discovery, the proof of the artificial transmutation of the elements, which has led to a wide extension of the field of radioactivity. A few words should first be said of the theoretical aspects of this problem as they appeared to me in 1918. On the nuclear theory, an atom could only be changed by altering in some way the charge or mass of the nucleus, or both together. It was known that the nucleus was of exceedingly minute dimensions with a radius of the order 10^{-12} cm. and must be held together by exceedingly powerful forces in order to prevent its spontaneous disruption. In order to transform an atom, it thus seemed clear that a very concentrated source of energy must be brought to bear on the individual nucleus. Actuated by these ideas, I began experiments in 1918 to test whether the bombardment of light elements by energetic α-particles might lead to the occasional transformation of a nucleus as the consequence of a direct collision between the

nuclei concerned. It could be calculated that in such an encounter the α-particle must come very close to the nucleus, even if it did not penetrate its structure. Such a close approach must in any case give rise to enormous forces between the α-particle and the nucleus which might be expected to produce such a distortion of its structure as to result in the disintegration of the nucleus. The scintillation method was employed to detect whether any fast particles appeared under such an intense α-particle bombardment. No effect was noticed for carbon or oxygen, but a number of fast particles were observed in the case of nitrogen, which were identified as swift hydrogen nuclei, now known as protons. It seemed clear that these protons could only arise as the result of the transformation of the nitrogen nucleus. In the light of later results, the essential processes involved in this transformation are now clear. Occasionally an α-particle actually enters the nitrogen nucleus and forms a new atom like fluorine of mass 18 and nuclear charge 9. This new nucleus is unstable and instantly breaks up with explosive violence, hurling out a fast proton and leaving behind a stable nucleus corresponding to a stable isotope of oxygen of mass 17. On an average only one α-particle in 100,000 is effective in producing such a transformation.

With the help of Chadwick, it was soon found that 12 of the light elements could be transformed in a similar way with the emission in each case of protons, but with different speeds and numbers. Time does not allow me to discuss later important developments which have shown that groups of protons of different velocities are ejected from each element and which have proved that resonance levels exist within the struck nucleus favouring the capture of α-particles of definite speed. Further investigation led to a discovery by Chadwick in 1933 of great significance. The element beryllium when bombarded by α-particles does not emit protons but a new type of particle of mass about 1 and zero charge called the "neutron." This new particle has remarkable properties, since, owing to its absence of charge, it can pass freely through the structure of atoms. Occasionally, it collides elastically with a nucleus, which is set in swift motion, but sometimes it enters a nucleus and is captured by it. The marked efficiency of the neutron in produciug transformations in nitrogen, oxygen, and other light elements was early shown by the experiments of Feather and Harkins, and, as we shall see, has led to very wide developments in the last two years. Before, however, discussing these advances, I must refer to another discovery of outstanding importance made by M. and Mme. Curie-Joliot in 1933, in which they showed for the first time that veritable radioactive bodies could be artificially created by the bombardment of certain elements by α-particles. Before this observation, it had been supposed that a stable element or elements were always produced as the result of the atomic explosion. They observed that when boron was bombarded by α-particles, an unstable element was produced which broke up with the emission of fast positive electrons and behaved exactly like a radioactive body of half period 10 minutes. This radioactive body had the chemical properties of nitrogen and the scheme of transformation as given below :

$$^{10}_{5}B + ^{4}_{2}He \longrightarrow ^{13}_{7}N + \text{neutron}$$

$$\text{and } ^{13}_{7}N \longrightarrow ^{13}_{6}C + \text{positron}$$

Similarly they found that bombardment of aluminium gave rise to radio-phosphorus of half period 3·2 minutes, which also broke up with the emission of positrons. The formation of radioactive bodies in this way is of great interest, and the appearance of the positron in these transformations is very unexpected.

It was soon shown that artificial radioactive bodies could be produced in various elements not only by bombardment with α-particles but also by protons, neutrons, and deuterons. In particular, Fermi and his collaborators showed that neutrons were exceedingly effective in producing radioactive bodies by bombarding the heavier elements, and more than 50 of these radioactive bodies were soon discovered, each with a characteristic period of decay. In contrast to the radioactive bodies produced by the α-rays in light elements, in the case of the heavier elements, the radioactive body emitted during the transformation not positive but negative electrons. In a number of cases, the chemical properties of the radioactive body have been determined and the scheme of transformation made

clear, but obviously time will be required to make sure of the process of transformations in elements which consist of a number of isotopes.

Fermi made another observation of great interest when he found that in the case of some elements, slow neutrons were much more effective in producing transformations than fast ones. Slow neutrons can be readily produced by passing the fast neutrons formed in a transformation through a considerable thickness of hydrogen-containing material, for example, water or paraffin. This aspect of the problem is now under intensive investigation throughout the world, and certain general conclusions have been reached. For fast neutrons, the cross-section of the atom for capture of the neutron varies somewhat from element to element, but is of the order 10^{-24} cm.^{2}. For slow neutrons, however, the cross-section for capture for some elements may be from 100 to 10,000 times greater than for fast neutrons. For example, cadmium and boron readily absorb slow neutrons and a still stronger absorption is shown by europium and gadolinium. So marked is the effect of the latter that a layer a small fraction of a millimetre thick is almost a complete absorber for slow neutrons. It is natural to suppose that absorption of the neutrons in an element is a sign of its transformation, even though it may not be easy to obtain proof of the exact nature of the transformation. There is now clear evidence, as shown by Moon and others, that some of the slow neutrons which are effective have thermal velocities. Still more remarkable, absorption in some elements seems to take place over a small range of velocities, a result which may indicate that there are very low energy resonance levels in some nuclei.

The ease with which slow neutrons are able to enter the nucleus of even the heaviest elements has proved of great service. The use of the neutron as a projectile has disclosed the existence of 50 or more ephemeral elements of the radioactive type, representing unstable varieties of isotopes of the elements, and has thus much extended our knowledge of atomic species. Most of these unstable atoms appear to be transformed directly into a stable atom, but in the case of the heavier elements it is quite likely we may be able to produce radioactive atoms which may break up in a succession of stages like the atoms of uranium and thorium. M. and Mme. Joliot-Curie conclude that a radioactive element of this type is formed by the action of slow neutrons on thorium, but the evidence is yet not complete. It will be a matter of great interest if we are able to create in this way new radioactive families for study.

My time is too limited to discuss with any detail the large number of new types of transformation which can be brought about by using fast protons and deuterons as projectiles. In some cases, the element formed by the capture of the incident particle breaks up into fragments; in others, a new stable element is formed, and in others a radioactive element. The use of deuterons as projectiles has disclosed many new and interesting types of transformation, in which either a proton or a neutron is released. One of the simplest and most striking of these transformations is produced when deuterium is bombarded by its own ions. Oliphant and others have shown that two distinct types of transformation occur:

$$ {}^{2}_{1}D + {}^{2}_{1}D \longrightarrow {}^{1}_{1}H + {}^{3}_{1}H $$
$$ \text{or} \longrightarrow {}^{1}_{0}n + {}^{3}_{2}He $$

In one case, a fast proton and an isotope of hydrogen of mass 3 appear; in the other, a fast neutron and an isotope of helium of mass 3. The masses of these hitherto unknown isotopes can be deduced with confidence from a consideration of the energy changes. Both of these isotopes are believed to be stable. While ^{2}H and ^{3}H and ^{3}He appear in several other transformations, no certain evidence has so far been obtained of the isotope of helium ^{5}He. A stable isotope of beryllium of mass 8 is also formed in certain transformations as well as radioactive isotopes. It is worthy of note that apart from the mass 5, all the masses from 1 to 20 on the atomic scale are represented either by stable or by radioactive atoms.

Conservation of Energy in Transformations.

In the transformation of the light elements by bombarding particles, the energy released per atom is of the same order of magnitude as that observed in the radioactive bodies. In a

few cases, particularly when deuterons are employed, the release of energy is considerably greater, and α-particles are expelled with higher speeds than from the radio-elements. In some cases too, penetrating γ-rays are emitted of high quantum energy. For example, the bombardment of ^{7}Li by protons gives rise to intense γ-rays of quantum energy as high as 16 million electron-volts—five times greater than the most penetrating γ-rays from radioactive bodies.

It is in general believed that the principle of the conservation of energy holds in these nuclear reactions when account is taken of the change of mass in the system before and after transformation. The equivalence of mass and energy seems now well established. A decrease of mass dm of a system corresponds to an emission of energy c^2dm, where c is the velocity of light. This law of equivalence is well illustrated in the transformation of the lithium isotopes by protons and deuterons shown below :

$$^7\text{Li} + {}^1\text{H} \longrightarrow {}^4\text{He} + {}^4\text{He} \qquad (1)$$

$$^6\text{Li} + {}^2\text{D} \longrightarrow {}^4\text{He} + {}^4\text{He} \qquad (2)$$

The relative masses of the nuclei involved are known from the accurate measurements of Aston and Bainbridge by the mass-spectrograph. The difference between the masses on the left- and the right-hand side of equation (1) is 0·0181 on the atomic scale, corresponding to a change of energy of 17·1 million electron-volts. This is in close accord with the accurate measurements of Oliphant and others of the energy of the expelled α-particles, *viz.*, 17·1 million volts. Similarly, kinetic energies of the α-particles liberated in equation (2) are 22·5 million volts, and this is found to agree well with the change of mass of the system.

As far as our observations have gone, the conservation not only of energy but also of momentum and nuclear charge appears to hold in all nuclear reactions where the energy is liberated in the form of massive particles. In the cases, however, in which either positive or negative electrons are expelled in the transformation, there are certain difficulties in interpretation which have not yet been resolved.

The application of the law of conservation of energy to nuclear changes promises to give us very accurate and reliable data on the relative masses of the atomic nuclei—probably far more precise than we can hope to obtain by the mass-spectrograph, especially in the case of the heavier elements. The transformation data are in some cases inconsistent with the measurements of the masses by Aston and others, and a new scale of masses was recently suggested by Oliphant and Bethe which fit closely with observation. New measurements by Aston and others to fix the masses of the light elements with the greatest possible precision are now in progress, and it seems likely that the new values will be in much closer accord with those deduced from transformation data. It is noteworthy that practically every type of nuclear reaction takes place which is consistent with the laws of conservation, although the probability of the different reactions may vary widely. This is very well illustrated by the great variety of transformations that have been observed in the light elements like lithium, beryllium, or boron when bombarded by different types of particle.

Structure of Radioactive Nuclei.

The discovery of the neutron has much simplified our conception of the structure of nuclei, which are now believed to consist of neutrons and protons with probably helium nuclei as secondary units, composed of a very stable combination of two protons and two neutrons. These particles are contained in a minute nuclear volume with radius of the order 5×10^{-13} cm. which is surrounded by a high-potential barrier which prevents the escape of the particles. In the case of a heavy nucleus like that of uranium, where the potential barrier is very high, about 20 million volts, the α-particle has not sufficient energy to escape over the barrier. On wave-mechanical principles, however, there is a small but finite probability that the α-particle may escape through the barrier, carrying with it the energy which it possesses within the nucleus. Such a view gives a rational explanation of the spontaneous radioactivity shown by uranium and thorium and their products, and also accounts in a general way for the well-known Geiger–Nuttall empirical relation which shows

a close connexion between the speed of the expelled α-particle from an element and the period of its transformation. In addition, Gamow has shown that on the wave-mechanics a charged particle like a proton has a small probability of entering a nucleus even if its energy is much too small on classical views to approach close to the nucleus. This theory accounts for the observation that comparatively slow particles can cause transformations, and also for the increase of efficiency of transformation with rise of energy of the bombarding particle.

It is difficult to obtain convincing evidence of the relation, if any, between the two units of structure of the atom, the neutron and the proton. It is difficult to measure the mass of the neutron with accuracy, but the evidence indicates that it is slightly heavier than the mass of the proton. It appears likely that the proton and neutron are closely related and under some conditions are mutually interchangeable within the nucleus.

The expulsion of a negative electron from the nucleus may be connected with the change of a neutron into a proton, while the escape of a positive electron is connected with the reverse operation. The peculiarities of the emission of electrons, both positive and negative, from radioactive atoms may possibly be traced to this interchange.

Before any detailed theory of nuclear structure can be attempted, it is necessary to find the nature and magnitude of the forces at small distances between the various components of the nuclear structure. Important information on these points ought to be obtained from a close study of the scattering of protons and neutrons in hydrogen. In default of any complete theory, some of the outstanding features of the relation between nuclei—for example, the differences between even- and odd-numbered elements—can be explained in a general way by assuming special types of forces between the elementary particles.

The spontaneous transformation of the radioactive bodies gave us the negative electron and α-particle as constituents of nuclei; the study of artificial transmutation has given us in addition three new particles, the proton, neutron, and positive electron, as well as a host of new radioactive bodies. In addition, as we have seen, we owe our conception of isotopes to the study of the chemistry of radioactive bodies, and our views of the nuclear structure of all atoms to observations on the scattering of α-particles.

It is clear that the study of radioactivity, both old and new, has been extraordinarily fruitful in extending our knowledge of the nature and varieties of atoms and of the way in which one atom can be changed into another. Although much progress has been made in the last few years, much still remains to be done before we can hope to understand how the atoms have been built up from elementary particles or to grasp the significance of the relative abundance of the varieties of atoms in our earth.

ANNUAL GENERAL MEETING

THE ninety-fifth Annual General Meeting was held at the University of Bristol on Thursday, *16th April*, 1936, the President, Professor N. V. SIDGWICK, C.B.E., D.Sc., F.R.S., occupying the Chair.

At 3.45 p.m. Fellows and their guests were welcomed by Dr. Stanley H. Badock, Pro-Chancellor and Treasurer of the University, and entertained to tea. Fellows subsequently proceeded to the Small Chemistry Lecture Theatre where the business portion of the meeting was held at 4.15 p.m.

The notice summoning the meeting was read, and the President formally presented the Report of Council for 1935—1936, with the Balance Sheets and Statements of Accounts for 1935. (See pp. 519—532.)

The Treasurer, who was called upon by the President, dealt with the accounts in detail and stated that, though the *Journal* had cost £194 less than in 1934, the cost of Abstracts had increased by £454. The net cost of Abstracts (£4975) was the highest on record, and the number of Abstracts published in 1935 (16,655) was more than double that published in 1927 (8010). Whereas Abstracts had continued to increase in cost, proceeds from the sale of Abstracts had steadily declined from £2405 in 1929 to £1841 in 1934. In 1935, sales had shown for the first time for six years a small increase, the amount being £51. Even if this upward tendency were to continue, it could not be expected that the revenue from this source would be sufficient to compensate the Society for the expenditure involved in coping with the continually increasing subject-matter to be abstracted. Certain steps were being taken by the Bureau of Chemical Abstracts to deal with the position, but he feared that drastic action would become inevitable unless additional subsidies from outside sources were forthcoming. During the last three years the Society had spent some £3000 in excess of its income.

The Chemical Council, which was formed in July, was now actively at work, and had given effect to the condition that the maintenance of the Library should be shared equally by contributions from each individual Chemist who is a member of one, or more, of the three constituent bodies. During 1936, the Institute of Chemistry would contribute £646 10*s*. and the Society of Chemical Industry £443. The Chemical Council were also hoping to effect economies by centralising the printing and distribution of the respective publications of the three chartered bodies. Funds resulting from such economies and any contribution from the Chemical Council's funds would be most welcome.

Professor C. S. Gibson, who proposed the adoption of the Report and Accounts, said, after paying a tribute to the work of the Treasurer and of the Chairman and members of the Bureau of Chemical Abstracts, that the increasing difference between the cost of production and the proceeds from the sales of the "A" Abstracts was due to the fact that better Abstracts were obtainable, and that every effort should be made to improve the Abstracts both in comprehensiveness and in indexing. The motion was seconded by Professor J. L. Simonsen, and carried.

A vote of thanks to the Auditors, proposed by Dr. W. Wardlaw and seconded by Dr. F. Fairbrother was carried, and on a motion from the Chair, Dr. H. E. Cox, Dr. H. D. K. Drew, and Dr. G. Senter were elected Auditors for the ensuing year.

Professor W. E. Garner, in proposing a vote of thanks to the Treasurer, Honorary Secretaries, Council and Committees for their services during the past year, referred in particular to the valuable services rendered by Professor S. Sugden during his term of office as Honorary Secretary from 1933–1936. This was seconded by Dr. E. B. Maxted, and carried with acclamation, Professor Sugden making brief acknowledgment.

The report of the Scrutators on the ballot for the election of Ordinary Members of Council (Town and Country Members) was presented, and elections were declared as follows :

Vice-Presidents, who have filled the office of President : Professor H. E. ARMSTRONG, Sir WILLIAM J. POPE.

Vice-Presidents, who have not filled the office of President : Mr. J. DAVIDSON PRATT, Sir ROBERT ROBERTSON, Professor R. ROBINSON.

Honorary Secretary : Professor J. W. COOK.

Ordinary Members of Council (Town Members) : Professor C. K. INGOLD, Dr. R. P. LINSTEAD, Dr. R. E. SLADE.

Ordinary Members of Council (Country Members) : Professor G. R. CLEMO, Mr. T. W. J. TAYLOR, Professor R. V. WHEELER.

A vote of thanks to the Scrutators (Dr. E. W. McClelland and Dr. W. H. J. Vernon) proposed by Dr. T. A. Henry and seconded by Dr. R. Raper was carried.

This concluded the business portion of the meeting. The company then assembled in the Large Chemistry Lecture Theatre.

The Longstaff Medal for 1936 was presented to Professor G. Barger, and in making the presentation the President said :

" Professor Barger, it is now my very pleasant duty to present to you the Longstaff Medal, which has been awarded to you by the unanimous vote of the Council.

" This Medal, which was established just 60 years ago, and is awarded every three years, is the highest distinction which the Society can bestow on one of its Fellows. You have well earned this distinction by the importance and extent of your researches on natural products of physiological interest. The most famous are those on ergot and its constituents, which form one of the first and still one of the most successful efforts to correlate physiological activity and molecular structure. But, in addition, you have increased our knowledge of a very large number of alkaloids, and synthesised many of them; in fact, there is no part of alkaloidal chemistry that you have not illuminated. The brilliant work of your pupil Harington on thyroxin also undoubtedly owes much to your inspiration.

" Further, through your wide circle of friends abroad, and your enviable command of foreign languages, you have done much to promote friendly intercourse between the chemists of all countries.

" It is therefore with great pleasure, and I am sure with the approval of all chemists, that I hand you the Longstaff Medal, and express the hope that you may continue to extend chemical knowledge with as much success as you have done in the past."

In returning thanks, Professor Barger said that he considered the award scarcely due to his own individual work, but rather a tribute to his associates in research, in whom he had been particularly fortunate. He was grateful for a long collaboration with Sir Henry Dale, for pupils such as the first recipient of the Harrison Memorial Prize, and for friendships with leaders in the field in which he had worked. The medal was a great stimulus to future effort.

In presenting the Harrison Memorial Prize for 1935 to Dr. Leslie E. Sutton, the President said :

" Dr. Sutton, in accordance with the unanimous decision of the Committee, which consists of the Presidents of the Chemical Society, the Society of Chemical Industry, the Pharmaceutical Society, and the Institute of Chemistry, I have much pleasure in handing you the Harrison Memorial Plaque and Prize. This Prize, which was founded in memory of an eminent Fellow of this Society who gave his life to the service of his country in the War, is awarded every three years to the Chemist under 30 years of age who shall have made the most meritorious original contributions to chemical science.

"Your work has already done much to increase our knowledge of molecular structure. It has helped to elucidate the formulæ of the bivalent carbon compounds, the oximes, and the azides; your paper on the relation between dipole moment and substitution in benzene derivatives is perhaps the most important contribution that has so far been made from the physical side to the problem of the dependence of reactivity in organic compounds on structure. Your later work on electron diffraction has also thrown light on important structural questions.

"I have very great pleasure, personal as well as official, in handing you the plaque and the prize, and I hope that your scientific career may continue to develop along the lines on which it has so auspiciously begun."

In thanking the President, Dr. Sutton expressed his appreciation of the great honour that had been conferred on him and said that he would like to echo Professor Barger's remarks in a humble way. He referred to the necessity of living up to the award and stated that if he were as fortunate with his collaborators in the future as he had been in the past, he hoped to be able to do so.

The President then delivered his Address entitled "Structural Chemistry." At its conclusion, a vote of thanks to the President for his services in the Chair during the past year and for his Address, with a request that he would allow it to be printed in the *Journal*, was moved by Professor F. Francis, seconded by Dr. J. T. Hewitt, and carried with acclamation, the President making acknowledgment.

A vote of thanks to the Chancellor, Council, and Senate of the University of Bristol for granting permission for the Anniversary Meetings and Dinner to be held in the University and for their hospitality was proposed by Professor W. N. Haworth, seconded by Professor J. E. Lennard-Jones, and carried with acclamation. This was acknowledged by Dr. Stanley H. Badock.

The President then moved a vote of thanks to the Reception and Executive Committees, mentioning in particular the Chairman (Dr. Stanley H. Badock), the Honorary Treasurer (Mr. Arthur Marsden) and the Honorary Secretary (Dr. E. B. Maxted), for their services in organising the meetings. This was carried unanimously.

REPORT OF COUNCIL, 1935—1936.

The year under review has been marked by a number of important events which will take their place in the history of the Society.

The Silver Jubilee of the Accession of His Majesty King George V to the Throne was celebrated in May, and a loyal Address of Congratulation was presented to His Majesty the King.

Towards the end of the Society's year, Britain and the Empire mourned the death of King George V. An Address of Condolence was presented to His Most Excellent Majesty King Edward VIII expressing the sense of deep personal loss which the President, Council, and Fellows of the Society felt in common with all His Majesty's subjects in the deeply lamented death of His Majesty King George V.

In June, the Councils of the three participating Bodies signed the Agreement setting up a Chemical Council. The activities of this Council are referred to later in the report; its institution is a large step forward in co-operation between the separate organisations of chemists.

The Society mourns the loss of two Past-Presidents, Professor H. Brereton Baker and Sir James Walker. Professor Baker, who was President from 1926 to 1928, died on the 27th April, 1935; he was elected a Fellow in June 1884, and served on the Council for 15 years. Sir James Walker, who was President from 1921 to 1923, died on the 6th May, 1935; he was elected a Fellow in February 1890, and served on the Council for 19 years.

I. *Honorary Fellows.*

The Council records with deep regret the death on the 14th March of Professor Arthur Hantzsch, who was elected an Honorary Fellow on the 17th October, 1929; and on the 13th December of Professor Victor Grignard, who was elected an Honorary Fellow on the 18th March, 1920.

On the 5th December, the Society elected as Honorary Fellows Professor J. N. Brønsted, Professor J. B. Conant, Professor Georg von Hevesy, Professor L. Ruzicka, and Professor G. Tammann, and the number of Honorary Fellows at the end of the year was 36.

II. *Chemical Council.*

The last report of Council contained reference to the advance made during the year in the negotiations for closer co-operation between The Chemical Society, The Institute of Chemistry, and The Society of Chemical Industry. A draft Agreement setting up a Chemical Council was circulated to Fellows in March, and on the 9th May an Extraordinary General Meeting was held at which the Agreement was approved. The Agreement in its final form was signed by the Councils of the three bodies in June.

The new Chemical Council is constituted of representatives of the three bodies concerned, and of representatives of Industry, the latter, for the present, being appointed by the Association of British Chemical Manufacturers.

The Chemical Council will administer a fund for the co-ordination of scientific and educational publications, the publication of new discoveries, the promotion of research, the maintenance of a library, and the provision and equipment of a suitable building or buildings for such purposes. The new Council, which has held several meetings, the first in July 1935, has formulated Standing Orders, has appointed Committees for various purposes, and has prepared an Appeal for the Fund, which is being raised for the purposes indicated above. It has also made progress with the consideration of the cost of publications for the chemical societies, the possibility of effecting economies, and other matters of interest and importance to the constituent bodies.

For the present, in view of the urgent need for further support for the publications and library of the Chemical Society, it has been agreed that the three Societies shall contribute, proportionately to their membership, to the cost of the maintenance of the library. This will indirectly help the Society to a substantial extent in supporting the burden of its publication of new knowledge and abstracts.

The Appeal for the Fund deserves the attention of all who are interested in chemistry and its applications in industry and commerce. Fellows who feel that they are able to assist in furthering the appeal are asked to communicate with the Honorary Secretary, The Chemical Council, 30, Russell Square, London, W.C. 1.

III. *Fellowship Statistics.*

The number of Fellows on the 31st December, 1934, was 3628. In 1935, 228 Fellows were elected and 21 reinstated, compared with 218 and 16, respectively, in 1934. The Society has lost 48 Fellows by death, 38 by resignation, and 66 by removal for non-payment of annual subscription, the corresponding figures last year being 50, 101, and 75, respectively.

The number of Fellows at the 31st December, 1935, was 3725, giving an increase of 97 over that at the end of 1934.

In previous years, it has been the practice to include in resignations the names of Fellows who had notified their intention to resign as from the 31st December of the year under review. Council decided last April that, in future, Fellowship statistics appearing in the Report of Council should relate to the financial year ending 31st December. Accordingly, the figures given above do not include names of Fellows resigning as from the end of 1935.

For purposes of comparison with the figures appearing in the last Report of Council, resignations should be increased to 101, thus decreasing the number of Fellows at the 31st December, 1935, to 3662, giving a net increase of 34 over that of the previous year.

IV. *Birthday and New Year Honours.*

The congratulations of the Society were conveyed to the following, whose names appeared in the lists of Birthday and New Year Honours :

Honorary Fellow.

Sir Frederick Gowland Hopkins	O.M.

Fellows.

Professor Shanti S. Bhatnagar	O.B.E.
Mr. Bryce C. Burt	Kt.
Professor Arthur Harden	Kt.
Dr. W. Lash Miller	C.B.E.
Dr. Frank T. Shutt	C.B.E.
Professor N. V. Sidgwick	C.B.E.
Dr. Frank S. Sinnatt	C.B.
Mr. Edward J. Wortley	C.M.G.
Mr. Charles A. Wrench	Kt.

V. *Fellows who have Completed 60 and 50 Years of Fellowship.*

The congratulations of the Society have been conveyed to the following Fellows, who have completed 60 years of Fellowship :

	Elected.
G. William Davey	November 18th, 1875.
J. F. M. H. Stone	December 2nd, 1875.
Sir Ernest H. Cook	December 2nd, 1875.
Bernard Dyer	December 16th, 1875.
John M. H. Munro	February 17th, 1876.

and to the following, who have completed 50 years of Fellowship :

	Elected.
Charles Watson	March 5th, 1885.
Walter Collingwood Williams	March 5th, 1885.
William Palmer Wynne	May 7th, 1885.
Thomas J. Greenway	June 4th, 1885.
Duncan S. Macnair	June 4th, 1885.
Sir Francis Newbolt	June 4th, 1885.
Robert Wallace	June 4th, 1885.
Hermann T. Vulté	November 19th, 1885.
John S. Adriance	December 3rd, 1885.
Matthew Hunter	December 3rd, 1885.
Charles Ranken	December 3rd, 1885.
Luther R. Scammell	December 3rd, 1885.

VI. *Journal.*

The *Journal* for 1935, containing 1907 pages (112 pages fewer than the *Journal* for 1934), consists of 434 memoirs (1744 pages), 33 notes (19 pages), 5 lectures (48 pages), a report on atomic weights (8 pages), the Presidential Address (17 pages), report of the Annual General Meeting (13 pages), and Obituary Notices (58 pages).

During 1935, 517 papers were received; of these, 14 were declined. Of the 434 memoirs published, 131 deal with General, Physical, and Inorganic Chemistry, and 303 with Organic Chemistry.

The average interval between the receipt and the publication of the papers in 1935 was 9·8 weeks (9·5 weeks for 1934; 9·4 weeks for 1933).

The recommendations contained in the report of the Special Committee on the Nomenclature of the Isotopes of Hydrogen adopted by Council on the 21st March appeared in the *Proceedings* for April (p. 31) and were communicated to the American Chemical Society.

VII. *Bureau of Chemical Abstracts.*

Six Meetings of the Bureau were held during the year, at one of which the Assistant Editors were present.

Abstracts. The appended table shows the number and average length of abstracts in Sections " A " and " B " published during 1935, the figures for 1934 being included for comparison.

	Abstracts A.				Abstracts B.			
	1934.		*1935.*		*1934.*		*1935.*	
	No. of Abs.	Pages.	No. of Abs.	Pages.	No. of Abs.	Pages.	No. of Abs.	Pages.
1st quarter	3,586	338	4,630	422	3,714	286	3,326	272
2nd ,, ...	3,946	372	4,114	376	3,486	272	3,846	304
3rd ,, ...	3,653	340	4,056	384	3,716	288	3,596	288
4th ,, ...	3,896	372	3,855	370	3,409	272	3,926	304
	15,081	1,422	16,655	1,552	14,325	1,118	14,694	1,168
Average length per abstract	0·19 Col.		0·19 Col.		0·16 Col.		0·16 Col.	

The 16,655 "A" Abstracts comprised 7601 in General, Physical, and Inorganic Chemistry, 519 in Geochemistry, 2617 in Organic Chemistry, and 5918 in Biochemistry. The corresponding figures for 1934 were 6929, 405, 2823, and 4924.

Of the 14,694 " B " abstracts, 8351 were from Journal literature and 6343 were abstracts of Patents (in 1934 : 7025 and 7300 respectively).

For reasons indicated in our last Report, the numbers of abstracts published continne to increase. Part of the expansion is, however, due to the fact that the literature is being more exhaustively covered than in the past.

The Biochemistry section again shows a greater percentage increase than the other sections. The position is being fully reviewed by the Chemical Society, and as a temporary expedient the Bureau has been asked to reduce the volume of Biochemistry abstracts published in 1936 to 10 per cent. less than that which appeared during 1935.

Steps have been taken during the year to improve the character of the abstracts in organic chemistry by including a concise statement of the general trend of the investigations where the nature of the original demands it.

The practice of using Roman letter symbols to denote other than chemical compounds has been found to render the abstracts obscure, and it has therefore been decided to confine the use of such symbols entirely to chemical compounds, and even in these cases to discontinue their use as far as possible.

As from the beginning of 1936 the classes in the " A " Abstracts will bear numbers as indicated in the revised Foreword published in the January issues. The corresponding numbers will appear at the top of the appropriate pages in the abstracts in order to facilitate reference to particular subjects.

Editorial Staff. The Bureau deplores the loss, by the death of Dr. H. W. Dudley, of one who had served most efficiently as Assistant Editor of Biochemistry Abstracts since 1924.

Dr. J. H. Birkinshaw has been appointed Assistant Editor to succeed Dr. Dudley, and will be assisted in the work by Dr. F. O. Howitt and Mr. A. G. Pollard.

Annual Index. The joint Annual Index of the abstracts for 1934 covered 692 pages, as compared with 640 pages for the 1933 Index. The cost of printing the Index was £1343 16*s*. 0*d*. and of the paper £259 13*s*. 7*d*. (corresponding figures for the 1933 Index were £1248 6*s*. 9*d*. and £244 3*s*. 4*d*.). The total number of entries in the Index increased from 87,675 in 1933 to 97,050 in 1934. Steps are being taken to ensure that the Index will appear considerably earlier than in the past.

Decennial Index The Subjects volume of the Decennial Index 1923–1932, comprising 1766 pages, was published in the early part of the year.

The press notices of the work were very gratifying, and the sales have been greater than was anticipated, 809 subscriptions having been received to the end of 1935. The grants from the two Societies were more than sufficient to cover the balance of the cost of production, after deducting revenue from sales, and the Bureau was able to refund the sum of £45 to the Chemical Society, and £245 to the Society of Chemical Industry (the latter having provided £200 more than the Chemical Society towards the cost).

Subscriptions are still being received, and the balance will be divided equally between the two Societies from time to time.

VIII. *Library.*

Excluding the evenings on which meetings of the Chemical Society were held, there were 8156 attendances during the year, as compared with 8549 in 1934. Of these 5128 were made by Fellows of the Chemical Society, and 3028 by Members of Contributing Societies, as against 5367 and 3182 in 1934.

The number of books borrowed was 5509, against 5525 in the previous year; of these 1378 were issued by post, compared with 1345 in the preceding year.

The Library telephone facilities are still extensively used, and the incoming calls included 852 inquiries which necessitated reference to books in the Library, as against 758 the previous year.

The additions to the Library comprise: 203 books, of which 94 were presented; 662 volumes of periodicals, and 233 pamphlets; as against 197 books, 674 volumes of periodicals, and 255 pamphlets last year.

The total number of volumes added during the year was 865. The Library now contains 39,675 volumes, consisting of 12,020 books and 27,655 bound volumes of periodicals.

Council records its thanks to Dr. T. A. Henry for the valuable services he has rendered to the Society as Chairman of the Library Committee from 1931 to 1935. Dr. O. L. Brady succeeded him in this office.

Council also expresses thanks for gifts received from Fellows, Authors, and Publishers during the year, and to Miss F. M. G. Micklethwait, Professor C. S. Gibson, Dr. E. W. Maddison, and a number of Publishers for continuing to present periodicals as issued.

IX. *General.*

Vacancies on Council.

Two vacancies on the Council have occurred during the year. Professor H. E. Armstrong was appointed to the vacancy among Vice-Presidents who have filled the office of President caused by the death of Sir James Walker, and Professor R. Robinson was appointed to the vacancy among Vice-Presidents who have not filled the office of President due to Professor N. V. Sidgwick being elected President. These appointments terminate at the Annual General Meeting in April.

Secretaryship.

In December the Council received with regret the resignation of Professor S. Sugden from the office of Honorary Secretary as from the next Annual General Meeting, and has recorded its appreciation of the valuable services he has rendered to the Society since assuming office in July 1932. Professor J. W. Cook has accepted Council's nomination to the office of Secretary.

Scientific Meetings.

Three special lectures have been held in London during the year. On the 28th February, Dr. A. S. Russell gave the Curie Memorial Lecture at the Royal Institution; on the 14th November, Dr. S. I. Levy gave the Brauner Memorial Lecture; and on the 12th February,

Lord Rutherford of Nelson gave the Sixteenth Faraday Lecture, entitled " Radioactivity and Atomic Theory," at the Royal Institution. The Haber Memorial Lecture by Professor J. E. Coates, arranged for the 23rd May, which was postponed owing to the illness of the lecturer, will be given during next session.

Twenty-four lectures were held outside London, and in addition Fellows were invited to attend three Bedson Lectures at Newcastle-on-Tyne. Five Discussions were held in London and four outside London. Nine Ordinary Scientific Meetings were held in London at which twenty-nine papers were read and discussed, and one was held at the University Chemical Laboratories, Cambridge, at which three papers were read and discussed. Meetings for the reading of Papers were also held at Leeds and Newcastle-on-Tyne.

A complete list of the lectures and discussions is given in the appendix to this Report.

Anniversary Meetings.

A report of the ninety-fourth Annual General Meeting at Burlington House on the 28th March was published in the *Journal* for April, and a brief account of the Anniversary Dinner held the same day at Grosvenor House appeared in the *Proceedings* for that month.

The Council has accepted an invitation from Fellows resident in Bristol to hold the Anniversary Meetings in the University of that city on the 16th and 17th April, 1936.

Longstaff Medal and Harrison Memorial Prize.

The Council has awarded the Longstaff Medal for 1936 to Professor G. Barger. The presentation of this medal and of the Harrison Memorial Prize, awarded by the Harrison Memorial Prize Selection Committee to Dr. L. E. Sutton, will be made at the Annual General Meeting in Bristol on the 16th April, 1936.

Representatives of the Society on other Bodies.

Association of British Chemical Manufacturers :
Professor W. A. Bone on Joint Committee dealing with Patents and Designs Act, and Medical Patents.

Association of Scientific and Technical Institutions :
Professor J. F. Thorpe on Council of Management.

Bristol University :
Professor F. G. Donnan on Court.

British Standards Institution :
Professor W. A. Bone on Council of the Chemical Division.
Dr. U. R. Evans on Committee to consider the question of preparing specifications for materials and plant used in electro-plating.
Drs. J. J. Fox and E. B. Hughes on Committee on Standardisation of Scientific Glassware.
Mr. A. L. Bacharach on Committee on Standards for Use in Dairying Chemistry.
Dr. A. D. Mitchell on Committee to prepare a British Standards Specification for Chemical Symbols and Abbreviations.

Bureau of Chemical Abstracts :
Mr. F. P. Dunn, Mr. A. J. Greenaway, Dr. J. T. Hewitt, Professor S. Sugden, and the Treasurer.

Chemical Council :
Professor N. V. Sidgwick (President), Professor I. M. Heilbron, and Professor G. T. Morgan.

City and Guilds of London Institute :
The President on Council.

Federal Council for Chemistry (until 31st December, 1935) :
Sir William J. Pope, Professor S. Sugden, and Professor J. F. Thorpe.

British National Committee for Chemistry (as from 1st January, 1936) :
The President, the Treasurer, and the Senior Secretary.

Home Office Air Raid Precautions Department to consider protection of population against hostile air attack :
Mr. J. Davidson Pratt.

Representatives of the Society at Public Functions.

Tercentenary Celebrations of the Muséum National d'Histoire Naturel (Paris, June 24th to 28th). Prof. A. Béhal.

Canadian Chemical Convention (Kingston, June 4th to 6th).	Dr. Léon Lortie.
Associazione Italiana di Chimica Fifth National Congress of Pure and Applied Chemistry (Sardinia, May 1st to 7th).	Prince Ginori Conti.
University of Warsaw, Meeting held to commemorate Madame Curie's services to Science (Warsaw, April 1st).	Dr. R. Truszkowski.
Fifteenth Congress of Industrial Chemistry (Brussels, Sept. 22nd to 28th).	Dr. E. B. Hughes.
Opening of the Rubber Exhibition organised by the Rubber Growers' Association (Manchester, June 4th).	Dr. R. H. Pickard.
Opening of a New Museum of Practical Geology (London, June 3rd).	Prof. C. S. Gibson.

Local Representatives.

A meeting of Local Representatives was held at the Imperial College (London) on the 29th March, at which it was reported that the steps already taken for increasing the activities of the Society were working satisfactorily. Various suggestions for increasing their usefulness were considered, and a memorandum defining the duties and activities of Local Representatives was approved.

Acknowledgments.

The Council expresses cordial thanks to all those Fellows who have served the Society in many ways, and would especially mention members of Committees, referees of papers submitted for publication, contributors to the Annual Reports, lecturers, Fellows who have opened discussions, and Local Representatives.

The Council has received volumes of the Society's publications from Mr. C. R. Beck, Mrs. Cockburn, Mr. A. J. B. Cooper, Dr. E. L. Kennaway, Mr. Frank Moul, Mr. O. J. W. Napier, Mrs. F. L. Overend, and Mr. C. Wyatt-Edgell, and records its thanks for these gifts.

X. *Financial.*

General Purposes Account.

Expenditure has exceeded income by £1642, the adverse balance in 1934 being £825. Expenditure is up by £809. This increase is mainly due to cost of administration, meetings, and local representatives, £187; a contribution towards the cost of the decennial index, £488, and legal and incidental expenses in connection with the formation of the Chemical Council and the consequent alteration of the Bye-Laws, £107.

Publications Fund.

Sales of publications and proceeds from advertisements have realised £228 more than in 1934; expenditure on the *Journal* was less by £193, but £453 more was spent on the *Abstracts* than in 1934.

Investments.

£1142 16*s*. New South Wales 3% Stock 1935 (Research Fund Account) was repaid at par. This, together with £90, the proceeds of a bequest from the late Dr. H. M. Atkinson, was invested in Conversion 3½ % Stock, 1961.

General.

The following contributions have been received:

£700 from the Government Publications Grant (through the Royal Society).
£200 from Imperial Chemical Industries, Ltd.
£25 from Mr. W. R. Criper to the Publications Fund to commemorate the King's Silver Jubilee.
£5 from Mr. W. Collingwood Williams to General Purposes Account to commemorate his jubilee of Fellowship.
£5 from Dr. G. McGowan to the Library.
£3 from Sir Prafulla C. Rây to the Library.

The Council records its thanks for these gifts and to those Fellows who continue to subscribe to the Publications Fund.

Research Fund.

In December applications for grants for research were received amounting to £101ξ from 93 Fellows and to £42 10*s*. from 4 non-Fellows. Grants amounting to £740 wer allotted.

The Council has received a bequest of £100 from the Executors of the late Dr. H. M Atkinson.

APPENDIX.

Discussions held in London.

21st March, on "Recent Progress in the Chemistry of the Terpenes," opened by Professor J. L. Simonsen; 16th May, on "The Significance of Phosphoric Esters ir Biochemical Processes," opened by Professor R. Robison; 21st November, on "Som Aspects of the Interaction between Gases and Solids," opened by Professor E. K. Rideal 16th January, on "Stereochemistry," opened by Dr. W. H. Mills, and 20th February a joint discussion with the Faraday Society on "The Kinetics of Gaseous Combustion," opened by Dr. R. G. W. Norrish.

Discussions held outside London.

Manchester. At the College of Technology and Engineers' Club: 6th December (join meeting with the Food Group of the Society of Chemical Industry and the Mancheste Section of the Society of Chemical Industry), a symposium on "Micro-organisms an Foodstuffs."

Oxford. At the Department of Biochemistry: 26th October (joint meeting with th Oxford University Alembic Club), on "Aromatic Character," opened by Professor R Robinson, Dr. W. H. Mills, Dr. W. G. Penny, and Dr. L. E. Sutton.

Sheffield. At the University: 8th February (joint meeting with the Yorkshire Branc of the Science Masters' Association), on "The Teaching of New Ideas in Chemistry i School and University."

South Wales. At University College, Cardiff: 22nd November, on "Some Problem of Sugar Chemistry in Relation to Biology," opened by Dr. E. L. Hirst.

Lectures held outside London.

Aberdeen. At the University: 17th May (joint meeting with the Institute c Chemistry and the Society of Chemical Industry) on "The Agricultural Utilisation c Peat Land," by Dr. Ian M. Robertson.

Birmingham. At the University, Edgbaston: 1st March, on "Recent Progress i Sesquiterpene Chemistry," by Professor J. L. Simonsen; 2nd December, on "Alkaloids—General Ideas and Methods," by Professor G. Barger; 9th December, on "The Decom position of Molecules by Light," by Dr. R. G. W. Norrish.

Edinburgh. At the North British Station Hotel: 23rd January, on "Some Recen Developments in Surface Chemistry," by Professor E. K. Rideal.

Glasgow. At the Royal Technical College: 15th March, on "From Governor Philli to d-*neoiso*Menthol, the Story of a Research, 1788—1934," by Professor J. Read; 7t February, on "Some Recent Developments in Surface Action," by Professor E. K. Ridea

Leeds. At the University: 14th October, on "The Fat-soluble Pigments of Nature," by Professor I. M. Heilbron; 31st January, on "The Formation of Nuclei in Solids an their Rate of Growth," by Professor W. E. Garner.

Liverpool. At the University: 27th February, on "Solid Reactions and Explosiv Decomposition," by Professor W. E. Garner; 18th October, on "Some Recent Advance in Stereochemistry," by Dr. W. Wardlaw; 10th December, on "Formation of Antho cyanins in Plants," by Professor R. Robinson; 7th February, on "The Play of th Molecules in a Simple Chemical Reaction," by Professor H. M. Dawson.

Manchester. At Manchester Central Library: 10th October (joint meeting with th

Manchester Section of the Institute of Chemistry and the Society of Chemical Industry), on "*Modern Structural Chemistry*," *by Professor N. V. Sidgwick. At the University*: 26th November (joint meeting with the University of Manchester Chemical Society), on "The Calcification of Animal Tissues," by Professor R. Robison. At the Engineers' Club: 10th January (joint meeting with the Manchester Sections of the Institute of Chemistry and the Society of Chemical Industry), on "A Chemical Contribution to the Cancer Enigma," by Professor J. W. Cook. At the University: 4th February (joint meeting with the University of Manchester Chemical Society), on "The Structure of Benzene," by Professor C. K. Ingold. At Manchester Central Library: 20th February (joint meeting with the Manchester Sections of the Institute of Chemistry and the Society of Chemical Industry), on "Chemistry and Medicine," by Dr. J. F. Wilkinson.

Newcastle and Durham. Bedson Lectures at Armstrong College: 8th November, on "Carcinogenic Hydrocarbons and their Effects," by Professor J. W. Cook; 6th December, on "Modern Theory of Valency," by Professor J. E. Lennard-Jones; 21st February, on "The Application of *X*-ray Diffraction to Chemistry," by Mr. J. D. Bernal.

North Wales. At University College, Bangor (joint meetings with the University College Chemical Society): 1st November, on "Thermodynamics and Reaction Velocity," by Professor M. Polanyi; 7th February, on "Ergot and Ergotism," by Professor G. Barger.

Sheffield. At the University: 15th March, on "The Simplest Free Radicals," by Professor F. Paneth; 29th November, on "Some Modern Views on Chemical Reaction Velocity," by Professor M. Polanyi.

South Wales. At University College, Swansea: 21st March, on "Recent Work on Molecular Structure," by Professor N. V. Sidgwick; 8th November (joint meeting with the University College of Swansea Chemical Society), on "Recent Investigations in the Chemistry of Gold," by Professor C. S. Gibson.

INCOME AND EXPENDITURE GENERAL PURPOSES ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1935.

1934 £ s. d.	1934 £ s. d.	Income.	1935 £ s. d.	1935 £ s. d.
	55 10 0	To Life Composition Fees		75 0 0
		„ Annual Subscriptions:—		
954 5 5		Received in advance, on account of 1935 ...	888 3 0	
7498 10 4		„ during 1935 „ „ ...	7057 10 0	
465 1 0		„ „ „ „ 1934 ...	369 4 3	
59 18 0		„ „ „ „ 1933 and previous years	20 0 0	
8970 14 9			8934 17 3	
375 0 0		*Less* amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	350 0 0	
8595 14 9			8584 17 3	
350 0 0		*Add* Arrears at date: £546 7*s.* 0*d.* Estimated to realise as per Balance Sheet	350 0 0	
	8945 14 9			8934 17 3
	771 18 8	„ Dividends on Investments		796 6 4
	250 2 0	„ Income Tax recovered		226 15 6
	26 16 10	„ Interest on Deposit		14 18 2
	— — —	„ Donation		5 0 0
	55 10 7	„ Miscellaneous Receipts		64 9 6
	825 1 10	„ Excess of Expenditure over Income carried to Balance Sheet		1642 0 1
	£10,930 14 8			£11,759 0 10

1934 £ s. d.	1934 £ s. d.	Expenditure.	1935 £ s. d.	1935 £ s. d.
		By Administration Expenses:—		
1934 4 7		Office Salaries and Wages	1978 6 3	
229 13 2		Superannuation	236 16 8	
194 17 1		House Expenses, etc. (proportion)	214 3 8	
52 10 0		Accountants' Charges	52 10 0	
243 8 6		Miscellaneous Printing and Stationery (proportion)	279 15 1	
151 12 4		Postages	167 8 3	
39 8 6		Miscellaneous	62 12 0	
	2848 14 2			2991 10 11
	148 2 3	„ Expenses of Meetings		163 2 10
		„ Donations:—		
50 0 0		Federal Council	— — —	
5 5 0		British Standards Institution	5 5 0	
2 2 0		Wollaston Plaque	— — —	
	57 7 0			5 5 0
	5868 18 9	„ Contribution to Publications Fund		5906 0 4
	55 10 0	„ Transfer to ditto (Life Composition Fees) ...		75 0 0
	1825 12 1	„ Contribution to Library Fund		1809 10 4
	76 14 8	„ Transfer to Staff Pensions Fund		74 16 3
	— — —	„ Transfer to Special Publications Fund for Collective Index, 1923–32		488 3 11
	49 15 9	„ Expenses of Local Representatives		78 15 5
	— — —	„ Expenses of formation of the Chemical Council		42 17 10
	— — —	„ Legal Expenses in connection with alterations to the Bye-Laws...		64 5 0
	£10,930 14 8			£11,759 6 10

INCOME AND EXPENDITURE ACCOUNTS OF OTHER FUNDS FOR THE YEAR ENDED 31ST DECEMBER, 1935.

PUBLICATIONS FUND.

1934 £ s. d.	1934 £ s. d.	Income.	1935 £ s. d.	1935 £ s. d.
		To Publication Sales (including back numbers):—		
2329 17 9		Journals and Proceedings	2479 19 2	
1840 11 7		Abstracts	1891 15 7	
13 8 0		Collective Index, Vols. I–VI	22 7 6	
— — —		Do. Vol. VII	45 0 0	
879 7 7		Annual Reports on Progress of Chemistry ...	858 5 0	
1 13 1		Other Publications	2 8 6	
254 9 4		Cheap sets	151 19 7	
	5312 1 4			5451 15 4
530 13 8		„ Proceeds of Advertisements	663 6 6	
153 11 1		*Less* Commission	197 15 6	
	377 2 7			465 11 0
	55 10 0	„ Transfer from General Purposes Account, being Life Composition Fees for year		75 0 0
	339 10 6	„ Donations		247 10 0
	700 0 0	„ Government Publications Grant (through the Royal Society)		700 0 0
	324 17 5	„ Dividends on Investments...		330 16 11
	102 4 0	„ Income Tax recovered		96 0 11
	11 1	„ Interest on Deposit		7 11
	5868 18 9	„ Transfer from General Purposes Account (the balance of expenditure on publications)		5906 0 4
	£13,080 15 8			£13,273 2 5

1934 £ s. d.	1934 £ s. d.	Expenditure.	1935 £ s. d.	1935 £ s. d.
		By Expenses on account of Journal:—		
1159 13 9		Editorial Salaries	1150 9 7	
85 12 6		Superannuation	85 12 6	
85 0 9		Editorial Postages	35 0 9	
3511 5 5		Printing, Paper, etc.	3367 13 4	
573 19 11		Distribution	562 11 0	
391 14 5		Authors' Copies	352 9 6	
17 11 5		Miscellaneous	18 10 2	
	5774 16 2			5581 6 11
		„ Expenses on account of Abstracts:—		
1302 12 0		Editorial Salaries	1318 3 6	
20 18 10		Superannuation	20 18 10	
79 1 3		Editorial Postages	77 5 8	
1402 7 9		Abstractors' Fees	1526 16 2	
3164 15 8		Printing, Paper, etc.	3453 7 2	
355 1 11		Distribution	376 12 3	
88 5 2		Miscellaneous	93 10 9	
	6413 2 7			6806 16 4
		„ Annual Reports on the Progress of Chemistry—		
727 2 11		Printing and Honoraria	727 10 2	
10 2 0		Advertising	22 9 0	
	737 4 11			749 19 2
		„ Carried to Balance Sheet of Publications Fund, viz.:—		
55 10 0		Life Composition Fees	75 0 0	
100 0 0		Donation: S. Melmore	— — —	
	155 10 0			75 0 0
	£13,080 15 8			£13,273 2 5

MM

INCOME AND EXPENDITURE ACCOUNTS OF OTHER FUNDS FOR THE YEAR ENDED 31ST DECEMBER, 1935.

LIBRARY.

1934 £ s. d.	1934 £ s. d.	Income.	1935 £ s. d.	1935 £ s. d.
		To Donations:—		
100 0 0		Association of British Chemical Manufacturers	100 0 0	
21 0 0		Biochemical Society	21 0 0	
15 15 0		Faraday Society	15 15 0	
25 0 0		Institute of Brewing	50 0 0	
250 0 0		Institute of Chemistry	250 0 0	
100 0 0		Society of Chemical Industry	100 0 0	
10 10 0		Society of Dyers and Colourists	10 10 0	
21 0 0		Society of Public Analysts	21 0 0	
3 0 0		Fellows	8 0 0	
23 4 10		Birmingham Dinner Committee	— — —	
	569 9 10			576 5 0
	3 17 8	" Miscellaneous receipts		8 10 11
	1825 12 1	" Contribution from General Purposes Account		1869 10 4
	£2398 19 7			£2454 6 3

1934 £ s. d.	Expenditure.	1935 £ s. d.
1325 14 11	By Salaries and Wages	1367 8 9
157 7 0	" Superannuation of Library Staff	162 16 0
615 5 7	" Books and Periodicals *	586 12 5
133 17 3	" Binding	137 1 6
46 12 2	" Printing, Stationery and Postages (proportion)	53 3 6
103 7 8	" House Expenses, etc. (proportion)	92 9 7
7 7 0	" Special Printing, etc. (Nathan Collection)	42 16 5
9 8 0	" Miscellaneous	11 18 1
£2398 19 7		£2454 6 3

* Other than those received in exchange.

RESEARCH FUND.

1934 £ s. d.	Income.	1935 £ s. d.
477 16 8	To Dividends on Investments	490 9 2
155 14 9	" Income Tax recovered	140 2 11
79 15 9	" Repayment of Grants	80 14 8
— — —	" Grants not applied for	10 0 0
2 13 5	" Interest on Deposit	1 13 2
— — —	" Sale of Apparatus	5 10 0
— — —	" Legacy	90 0 0
— — —	" Repayment at par of £1,142 16s. 0d. New South Wales 3% Stock	1142 16 0
— — —	" Balance, being Excess of Expenditure over Income, carried to Balance Sheet	17 7 6
£716 0 7		£1978 13 5

1934 £ s. d.	Expenditure.	1935 £ s. d.
672 8 0	By Grants	740 0 0
7 3 10	" Miscellaneous Expenses	5 17 5
— — —	" Purchase of £1,146 13s. 1d. Conversion Stock 3½%	1232 16 0
36 8 9	" Balance, being Excess of Income over Expenditure, carried to Balance Sheet	— — —
£716 0 7		£1978 13 5

SPECIAL PUBLICATIONS FUND.

1934 £ s. d.	1934 £ s. d.	Income.	1935 £ s. d.	1935 £ s. d.
		To Sales of Publications:—		
55 0 0		Abstracts "A" printed on one side of the paper	61 0 0	
9 7 6		Memorial Lectures, Vol. I.	11 1 6	
7 18 3		Do. Vol. II.	7 12 9	
17 19 6		Do. Vol. III.	7 16 11	
4 11 0		List of Fellows	3 0	
4 2 0		Portraits	8 3	
6 5 1		Faraday Lectures	5 4 6	
1 16 6		Perkin Memorial Volume	1 6 0	
10 0		Discussion Number	— — —	
6 3 0		Fourth Pedler Lecture	1 0	
— — —		Fifth Liversidge Lecture	8 0	
	113 12 10			95 1 11
	56 9 1	" Dividend on Investment		65 14 2
	2 6 3	" Interest on Deposit		2 0 4
	18 10 2	" Income Tax recovered		16 13 0
	£190 18 4			£179 9 5

1934 £ s. d.	Expenditure.	1935 £ s. d.
57 1 0	By Production of Abstracts "A" printed on one side of the paper	64 15 11
— — —	" Reprints for Memorial Lectures, Vol. IV.	3 13 0
8 8 5	" Do. of Fourth Pedler Lecture	— — —
— — —	" Do. of Fifth Liversidge Lecture	2 4 3
— — —	" Contribution towards the collected works of the late Sir William Hardy	37 10 0
125 8 11	" Balance, being Excess of Income over Expenditure, carried to Balance Sheet	71 6 3
£190 18 4		£179 9 5

SPECIAL LECTURES FUND.

1934 £ s. d.	Income.	1935 £ s. d.	1934 £ s. d.	Expenditure.	1935 £ s. d.
34 18 8	To Dividends on Investments ...	37 15 3	25 0 0	By Honorarium ...	25 0 0
11 7 2	" Income Tax recovered ...	10 4 6	22 6 5	" Lecture Expenses ...	9 16 0
7 2	" Interest on Deposit ...	6 0	— — —	" Miscellaneous Expenses ...	10 6
13 5	" Balance, being Excess of Expenditure over Income, carried to Balance Sheet ...	— — —	— — —	" Balance, being Excess of Income over Expenditure, carried to Balance Sheet ...	12 19 3
£47 6 5		£48 5 9	£47 6 5		£48 5 9

STAFF PENSIONS FUND.

1934 £ s. d.	Income.	1935 £ s. d.	1934 £ s. d.	Expenditure.	1935 £ s. d.
76 14 8	To Transfer from General Purposes Account ...	74 16 3	120 0 0	By Pension paid during 1935 ...	120 0 0
32 12 10	" Dividends on Investments ...	35 12 7			
10 12 6	" Income Tax recovered ...	9 11 2			
£120 0 0		£120 0 0	£120 0 0		£120 0 0

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

1934 £ s. d.	Income.	1935 £ s. d.	1934 £ s. d.	Expenditure.	1935 £ s. d.
40 8 9	To Dividends on Investments ...	41 1 3	— — —	By Advertising ...	3 4 0
12 11 0	" Income Tax recovered ...	11 5 11	53 14 6	" Balance, being Excess of Income over Expenditure, carried to Balance Sheet ...	50 3 2
14 9	" Interest on Deposit ...	1 0 0			
£53 14 6		£53 7 2	£53 14 6		£53 7 2

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31st December, 1935.

GENERAL PURPOSES.

1934 £ s. d.	1934 £ s. d.	Liabilities.	1935 £ s. d.	1935 £ s. d.	1934 £ s. d.	Assets.	1935 £ s. d.
	892 13 0	To Subs. received in advance ...		922 7 6	25,854 5 1	By Investments as per Schedule (cost or value when acquired) ...	25,854 5 1
	3,255 12 0	" Sundry Creditors (Printing and other Expenses) ...		4,372 4 2	446 9 9	" Sundry Debtors ...	407 8 4
23,675 9 9		" Excess of Assets over Liabilities as per last Balance Sheet ...	22,883 9 5		350 0 0	" Subscriptions in Arrear, £546 7s. 0d. Estimated to realise ...	350 0 0
825 1 10		*Deduct* Excess of Expenditure over Income for Year ...	1,642 0 1		380 19 7	" Cash in hand ...	41 5 5
22,850 7 11							
33 1 6	22,883 9 5	*Add* Transfer from Suspense Account unexpended balance ...	— — —	21,241 9 4			
	— — —	" Current Account at Bankers (overdrawn) ...		116 17 10			
	£27,031 14 5			£26,652 18 10	£27,031 14 5		£26,652 18 10

PUBLICATIONS FUND.

1934 £ s. d.	1934 £ s. d.	Liabilities.	1935 £ s. d.	1935 £ s. d.	1934 £ s. d.	Assets.	1935 £ s. d.
11,119 10 11		To Excess of Assets over Liabilities as per last Balance Sheet ...	11,275 0 11		11,226 3 10	By Investments as per Schedule (cost or value when acquired) ...	11,226 3 10
155 10 0	11,275 0 11	*Add* Amount transferred from Income and Expenditure Account for Investment ...	75 0 0	11,350 0 11	48 17 1	" Cash at Bank ...	123 17 1
				£11,350 0 11	£11,275 0 11		£11,350 0 11

1934 £ s. d.	1934 £ s. d.	Liabilities.	1935 £ s. d.	1935 £ s. d.	1934 £ s. d.	Assets.	1935 £ s. d.
	710 8 0	To Sundry Creditors		760 0 0	14,443 2 0	By Investments as per Schedule (cost or value when acquired)	14,675 18 0
14,447 9 1		„ Excess of Assets over Liabilities as per last Balance Sheet	14,483 17 10		751 3 10	„ Cash at Bank	783 8 4
— — —		Add Profit on Redemption of New South Wales 3% Stock	142 16 0				
— — —		„ Legacy	90 0 0				
			£14,716 13 10				
36 8 9		Add Excess of Income over Expenditure for year	— — —				
— — —		Less Excess of Expenditure over Income for year	17 7 6				
	14,483 17 10			14,699 6 4			
	£15,194 5 10			£15,459 6 4	£15,194 5 10		£15,459 6 4

SPECIAL PUBLICATIONS FUND

1934 £ s. d.	1934 £ s. d.	Liabilities.	1935 £ s. d.	1935 £ s. d.	1934 £ s. d.	Assets.	1935 £ s. d.
	35 0 0	To Amount prepaid for 1936		43 0 0	1600 0 0	By Investment as per Schedule (cost or value when acquired)	1600 0 0
	15 5 6	„ Sundry Creditors		25 4 6	682 16 8	„ Cash at Bank	460 16 7
577 2 9		„ Sinking Fund for Collective Index (1923–32) as per last Balance Sheet	311 5 4				
— — —		Add Transfer from General Purposes	488 2 11				
4 2 7		Interest	11 9				
581 5 4			800 0 0				
270 0 0		Less Paid on Account to Bureau of Chemical Abstracts	800 0 0				
	311 5 4			— — —			
1795 16 11		Excess of Assets over Liabilities as per last Balance Sheet	1921 5 10				
195 8 11		Add Excess of Income over Expenditure for Year	71 6 3				
	1991 5 10			1992 12 1			
	£2282 16 8			£2060 16 7	£2282 16 8		£2060 16 7

SPECIAL LECTURES FUND

1934 £ s. d.	1934 £ s. d.	Liabilities.	1935 £ s. d.	1935 £ s. d.	1934 £ s. d.	Assets.	1935 £ s. d.
1076 7 9		To Excess of Assets over Liabilities as per last Balance Sheet	1075 9 4		1000 0 0	By Investments as per Schedule (cost or value when acquired)	1000 0 0
— — —		Add Excess of Income over Expenditure for year	12 19 3		75 9 4	„ Cash at Bank	88 8 7
18 5		Less Excess of Expenditure over Income for year	— — —				
	1075 9 4			1088 8 7			
	£1075 9 4			£1088 8 7	£1075 9 4		£1088 8 7

STAFF PENSIONS FUND.

1934 £ s. d.	Liabilities.	1935 £ s. d.	1934 £ s. d.	Assets.	1935 £ s. d.
907 14 0	To Excess of Assets over Liabilities as per last Balance Sheet	907 14 0	902 13 9	By Investments as per Schedule (cost or value when acquired)	902 13 9
			5 0 3	„ Cash at Bank	5 0 3
£907 14 0		£907 14 0	£907 14 0		£907 14 0

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

1934 £ s. d.	1934 £ s. d.	Liabilities.	1935 £ s. d.	1935 £ s. d.	1934 £ s. d.	Assets.	1935 £ s. d.
— — —		To Sundry Creditors		1 2 6	1101 7 11	By Investments as per Schedule (cost or value when acquired)	1101 7 11
1165 11 4		„ Excess of Assets over Liabilities as per last Balance Sheet	1219 5 10		117 17 11	„ Cash at Bank	169 3 7
53 14 6		Add Excess of Income over Expenditure for year	50 3 2				
	1219 5 10			1269 9 0			
	£1219 5 10			£1270 11 6	£1219 5 10		£1270 11 6

SCHEDULE OF INVESTMENTS.

GENERAL PURPOSES.

Nominal Details.	Cost or Value when Acquired. £ s. d.	Market Value 31st December, 1935. £ s. d.
£787 London, Midland and Scottish Railway 4% *Debenture Stock*	839 3 7	849 19 2
£1520 14s. 3d. Cardiff Corporation 3% Stock, 1914/54	1650 0 0	1520 14 3
£1400 India 2½% Stock	1316 1 0	1050 0 0
£2400 Bristol Corporation 2½% Debenture Stock, Bristol Dock Account	2070 2 0	2208 0 0
£2713 London, Midland and Scottish Railway 4% Preference Stock	3572 0 4	2251 15 10
£1200 Leeds Corporation 3% Stock	1143 1 0	1140 0 0
£1066 6s. 2d. Union of South Africa 3% Stock, 1954/64	1067 12 10	1107 5 5
£1200 London and North Eastern Railway 3% Debenture Stock ...	1033 11 0	984 0 0
£700 Canada 3½% Stock, 1930/50	704 8 6	707 0 0
£2529 6s. 9d. 5% Conversion Loan, 1944/64	2446 2 6	3035 4 2
£1100 5% ditto ditto ditto	1045 0 2	1320 0 0
£600 4% Funding Loan, 1960/90	480 0 0	702 0 0
£11,212 9s. 3½% Conversion Stock 1961, or after	8487 2 2	12,081 8 3
	£25,864 5 1	£28,957 7 1

PUBLICATIONS FUND.

Nominal Details.	Cost or Value when Acquired. £ s. d.	Market Value 31st December, 1935. £ s. d.
£6974 19s. 9d. 3½% Conversion Stock, 1961, or after	5508 12 8	7515 11 0
£3173 1s. 6d. 5% Conversion Loan, 1944/64	*3199 18 7*	*3807 13 10*
£817 P. & O. Steam Navigation Co. Deferred Stock...	2060 0 0	735 6 0
£608 London, Midland and Scottish Railway 4% Guaranteed Stock	457 12 7	621 1 10
	£11,226 3 10	*£12,679 12 8*

RESEARCH FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1935. £ s. d.
£1000 London and North Eastern Railway 4% 2nd Guaranteed Stock	1010 0 0	920 0 0
£1034 Great Western Railway 2½% Debentures	1049 15 11	754 16 5
£1122 Metropolitan Water Board 3% "B" Stock	1002 16 9	1088 6 9
£1483 London, Midland and Scottish Railway 4% Debenture Stock	1508 3 6	1601 12 10
£806 Victoria 3% Stock, 1929/49	706 6 2	789 17 7
£4498 11s. 5% Conversion Loan, 1944/64	4267 4 10	5398 5 2
£6311 6s. 10d. 3½% Conversion Stock, 1961, or after	5131 10 10	6800 9 5
	£14,675 18 0	£17,353 8 2

SPECIAL PUBLICATIONS FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1935. £ s. d.
2115 8s. 10d. 3½% Conversion Stock, 1961, or after	*£1600 0 0*	*£2279 7 9*

SPECIAL LECTURES FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1935. £ s. d.
£1299 9s. 4d. 3½% Conversion Stock, 1961, or after	£1000 0 0	£1400 3 6

STAFF PENSIONS FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1935. £ s. d.
£683 6s. 1d. 3½% Conversion Stock, 1961, or after	527 13 9	736 5 2
£371 17s. 1d. 5% Conversion Loan, 1944/64	375 0 0	446 4 6
	£902 13 9	£1182 9 8

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1935. £ s. d.
£61 15s. 8d. 3½% Conversion Stock, 1961, or after	50 1 5	66 11 4
£1255 London Midland and Scottish Railway 4% Debenture Stock	1051 6 6	1355 8 0
	£1101 7 11	£1421 19 4

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balances at the Bankers and the Investments. The figures relating to the Bureau of Chemical Abstracts are included in the above accounts subject to the production of certified accounts by the Bureau.

23, Queen Victoria Street, E.C. 4,
18th February, 1936.

W. B. Keen.
Chartered Accountant.

Approved { W. Morris Colles
Harry D. K. Drew
George Senter

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, April 16th, 1936.

By N. V. SIDGWICK, C.B.E., M.A., D.Sc., F.R.S.

Structural Chemistry.

THERE are two ideas about the progress of science which are widely prevalent, and which appear to me to be both false and pernicious. The first is the notion that when a new discovery is made, it shows the previous conceptions on the subject to be untrue; from which unscientific people draw the very natural conclusion that if to-day's scientific ideas show those of yesterday to be wrong, we need not trouble about them, because they may themselves be shown to be wrong to-morrow. It is difficult to imagine any statement more opposed to the facts. The progress of knowledge does indeed correct certain details in our ideas, but the main result of every great discovery is to establish the existing doctrines on a firmer foundation, and give them a deeper meaning.

The second false notion is that the progress of research involves increasing specialisation: and specialisation, we are told, means knowing more and more about less and less. This last phrase has undoubtedly brought comfort to many people who know practically nothing about absolutely everything. But it is entirely untrue that as knowledge grows, its conclusions are based on a uarrower range of observations. Nothing is more remarkable in the immense development of physics and chemistry during this century than the way in which it has brought to bear on the same problems the results of the investigation of widely different properties, obtained by widely different experimental methods.

These points are well illustrated by the subject I have chosen for my remarks to-day—the development of structural chemistry from its origin to the present time. We do not always realise what a remarkable history this theory has had. It was laid down in the 50's and 60's of last century, mainly through the work of Kekulé and Cannizzaro; it was extended to three dimensions by van 't Hoff and Le Bel in 1874, 62 years ago. Since then, at any rate until the last three or four years, it has undergone no serious modifications. A few minor developments have been introduced, such as the recognition of the distinction between ionised and non-ionised links, and of the co-ordinate or semipolar bond. But in essence it remains to-day what it was 60 years ago, and Cannizzaro, if he read the last (1935) volume of Richter's textbook, would find no difficulty in understanding the formulæ and the equations.

This structural theory is of extreme simplicity. It assumes that the molecule is held together by links between one atom and the next: that every kind of atom can form a definite small number of such links: that these can be single, double, or triple: that the groups may take up any position possible by rotation round the line of a single but not round that of a double link: finally that with all the elements of the first short period, and with many others as well, the angles between the valencies are approximately those formed by joining the centre of a regular tetrahedron to its angular points. No assumption whatever is made as to the mechanism of the linkage.

Through the whole development of organic chemistry this theory has always proved capable of providing a different structure for every different compound that can be isolated. Among the hundreds of thousands of known substances, there are never more isomeric forms than the theory permits.

At the same time our knowledge of the meaning of these structures has developed, especially in the last 20 years, to an enormous extent. We have applied to their investigation a whole series of physical methods, based on the examination of the absorption spectra in the infra-red, the visible, and the ultra-violet, and of the Raman spectra: on the measurement of specific heats and heats of combustion, of the dielectric properties, and of the scattering of X-rays and electron waves, as well as on the study of chemical dynamics: to mention only the most important. To Kekulé the links had no properties beyond that of linking; but we now know their lengths, their heats of formation, their

resistance to deformation, and the electrostatic disturbance which they involve. Throughout all this work the starting point has always been the structural formula in the ordinary organic sense. There is no better example of the effect of new discoveries in giving new meaning to a theory while they leave the truth of the theory unaffected, and of the way in which modern research, instead of being content with evidence of one kind, as were the older organic chemists with that of chemical reaction, draws its material from every side, and from every branch of chemistry and physics.

The position of the structural theory is peculiar both in its extent and in its limitations. In predicting the number of isomeric forms that can exist it is infallible; it may not always be possible to obtain all the forms, for the theory says nothing about stability, but wherever a new form can be obtained, there is a new formula ready for it. On the other hand the theory gives a very limited representation of the properties of the linked atoms, and in particular of the reactivity. We write the link of carbon to chlorine in the same way C–Cl in chlorobenzene, where the chlorine can scarcely be removed by anything short of metallic sodium, and in acetyl chloride, which is hydrolysed almost explosively by water. In fact we know that the properties of a link are not determined solely by the atoms which form it (which are all that the structural theory takes into account), but are modified by all the other atoms in the molecule.

In the light of modern knowledge it should be possible to explain both the successes and the failures of the theory. We may take the successes first—the power which the theory has of predicting the number of separable isomeric forms of a molecule which can exist. If a compound is to be separable, it must not change as soon as it is formed into something else; we may fairly say that unless a molecule lives in one form for a few seconds, before it changes over into another, the two will be regarded as one substance. Now we know that if a change is slow, that is because the molecules need to acquire extra energy before they can react. Recent work, especially that of Eyring and Polanyi, has shown that this extra energy—the heat of activation—is mainly devoted to stretching the links so as to bring the atoms into the positions required for the production of the new molecule; the consequent rearrangement of the electronic orbits takes place relatively easily. Hence the change from one form to another will occur the more rapidly, the less the differences of position of the atoms in the two molecules : if this difference is very small, the change will occur at once, and we shall not be able to separate the less stable form at all. Thus the number of separable forms is the number of different arrangements in space of the atoms that are possible.

It would seem, then, that the structural theory owes its success to the fact that it prescribes all the possible arrangements in space that a given group of atoms can assume. This conclusion is entirely supported by the physical evidence. We know that the distance between two linked atoms is a very constant magnitude; it is very little affected by the other atoms in the molecule; it is only reduced about 10% by the conversion of a single link into a double or of a double into a triple. Recent work has indeed shown that these distances are capable of certain highly significant modifications, to which I shall return later, but these also are all small—of the order of 10%. Also the valency angles are fairly constant; on the tetrahedral theory, that between two single links is 110°, and that between a single link and a double 125°. The experimental evidence shows that the establishment of a covalent link between two atoms, which is the foundation of the structural theory, is actually the fundamental process in molecular structure, and that its dimensions are little affected by variations in the rest of the molecule.

The conclusions of wave mechanics are in support of this view, and at the same time go far to explain the failure of the structural theory to account for the variations in reactivity. The complete calculation of the properties by wave mechanics is not yet possible except for a few of the simplest molecules, but by a variety of approximations and short cuts we can arrive at something more than a qualitative solution of the structural problem in general: we can get a picture of the mechanism by which the atoms are held together in a molecule, and what we find is this. The primary covalent linkage can be explained as being due to the sharing of two electrons between the atoms, as Lewis supposed, and moreover the theory provides a mechanism for this sharing, which the earlier theory

did not; this forms the most important part of the interatomic forces, but it can be shown that it is not sufficient to take into account the reaction of each electron with the two particular adjacent nuclei, and that we have to consider the effect of all the electrons on all the nuclei in the molecule: in other words there is a force—a kind of bond—between every atom and every other. This is in entire agreement with our chemical experience, which shows that the properties of any particular link are to some extent dependent on all the atoms in the molecule.

Thus both the theoretical and the experimental evidence lead to the conclusion that in the formation of a molecule we have to distinguish two factors: first, the simple linkage between the atoms, and, secondly, the further influence on these links of the other atoms in the molecule which are not directly attached. The first of these determines the positions of the atoms in space, and therefore, in accordance with what I have said, the individuality of the compound; it is this factor which is expressed in the ordinary structural theory, and that is why that theory is able to determine the number of possible—that is, isolable—forms. The second factor has a large effect on the reactivity of the molecule; it is not regarded by the structural theory, which therefore cannot make any statement about the reactivity, except in the organic sense of showing in what order the atoms are linked, which depends on the first factor and not on the second.

It is not indeed to be expected that any simple theory should express so complicated a phenomenon as the interaction of all the nuclei and all the electrons of a molecule with one another, which even in benzene is a 54- or at least a 42-body problem. The full theoretical solution must wait until the application of the equations of wave mechanics has been made much easier than it now is; and we shall have to wait a long time before this becomes possible for molecules of any complexity. At the same time we may hope that the progress of wave mechanics will give us new principles of structure and of reactivity which will be applicable even where a complete calculation cannot be carried out.

One such principle has already been discovered, and it constitutes the most important development of structural chemistry since the days of van 't Hoff. This is the principle of resonance, due originally to Hund, but applied to organic chemistry mainly by Pauling and his school. The conclusions of this theory can only be reached by wave mechanics, but they can fortunately be expressed in very simple terms.

It has long been known that if we synthesise substances with structural formulæ which are different, but which can pass into one another by a mere rearrangement of single and multiple links, without either separating two linked atoms, or joining two that were separate, we get the same substance, which has the reactions of both formulæ. The classical example is that of the two Kekulé formulæ for benzene. This is explained by the relation between reaction velocity and spatial position: the two structures will have their atoms in nearly the same positions, and so the rate of change will be very great.

But the resonance theory takes this much further. The equations of wave mechanics show that if a molecule can be represented, on the ordinary structural theory, by two different formulæ, then under certain conditions its actual state is not either one or the other, nor is it a mixture of the two in chemical (tautomeric) equilibrium, but it is a hybrid structure intermediate between them, which cannot be represented by the ordinary symbols and has to some extent the properties of both. This phenomenon is known as resonance; the name is a bad one, because it suggests that the molecule is oscillating between the two states, which is not true; it would be better to give it some such name as mesomerism, if that is not already otherwise occupied; but for the present we have to accept the terminology of the physicists.

The conditions which must be satisfied for the resonance to be possible are two: (1) the positions of the atoms in the two structures must be nearly the same; the actual positions in the hybrid will be somewhere between them, and so involve a certain amount of strain with respect to either, but this must not be large: (2) the stabilities of the two must not differ greatly, or, to put it crudely, neither structure must be too improbable. The state of the hybrid is not necessarily half way between the two structures: it lies nearer to the more stable one. The occurrence of the resonance produces two important physical effects. (I) The energy content of the molecule is smaller, or its stability greater, than that of either

form; this is of fundamental importance, because it follows that resonance must always *occur whenever it is possible under the conditions* (1) *and* (2). The resonance energy may be very considerable, amounting sometimes to as much as the energy of a single link (up to 70,000 calories). This affords one means of detecting the occurrence of resonance, since the heat of combustion of the hybrid must be smaller, or its heat of formation larger, than we should calculate for either of the two formulæ. (II) The second effect, which again is important for detecting the resonance, is that the linked atoms come rather nearer together than in either of the separate forms, owing to the greater strength of the link.

These wave-mechanical conclusions, as I have said, can only be reached by making certain assumptions and approximations, the validity of which cannot be judged by the non-mathematician, and so it is essential for us to check them by experiment. I will give one or two examples, in which the criteria are the heats of formation from the atoms, and the interatomic distances.

Carbon dioxide can have three formulæ, which are given below together with the calculated values of the distances and the heats of formation :

	O=C=O	O←C≡O	O≡C→O	Observed.
Distance	1·28 1·28	1·43 1·13	1·13 1·43	O . . . O
	2·56 A.	2·56 A.	2·56 A.	2·30 A.
Heat of formation (kg.-cals.)	348	*ca.* 350	*ca.* 350	380

These structures satisfy condition (1), because they are all linear, and the distances between the atoms do not differ much : and condition (2), because the heat of formation of the link of carbon to oxygen is very nearly proportional to its multiplicity, and the electrostatic disturbance produced by the co-ordination does not seem to have much effect on the energy. Resonance is therefore possible, and that it occurs is shown by the two characteristic results : (I) the heat of formation of the carbonyl group in aldehydes and ketones is 174 kg.-cals., and so that of O=C=O should be twice this, or 348 kg.-cals. : the observed value is 380, an excess of 30 kg.-cals. (II) The distance from oxygen to oxygen should be, in any of the three forms, 2·56 A. : it is found to be 2·30 A.

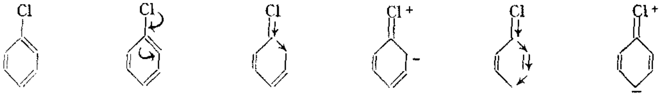
Many other examples could be quoted.* The most obvious are those in which there are two or more atoms similar except for a difference of linking, and where the resonance causes this difference to vanish. Thus the crystallographic evidence shows that the NO_3' and CO_3'' ions are plane structures, as the tetrahedral theory requires for the two formulæ $O{=}N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$ and $O{=}C\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}$; but it further shows that in both ions the three oxygen atoms are at the points of an equilateral triangle, with the nitrogen or carbon at the centre. It is clear that the three oxygens share the double link, which is not localised on any one of them. Here too we find the characteristic shortening of the link. The values are : for NO_3', N—O 1·36, N=O 1·22, mean 1·31; obs. 1·23; for CO_3'', C—O 1·43, C=O 1·28, mean 1·38; obs. 1·23.

There are many important applications of this theory, for example, to the co-ordination of hydrogen, to triphenylmethyl, to the triphenylmethane dyes and the *meri*-quinoid compounds in general, to the inactivity of the carbonyl group in acids and esters, and so forth, which I must pass over. But there is one application of such far-reaching importance that something must be said about it. The views of reactivity put forward by organic chemists during the last 20 years or so find in the theory of resonance their physical justification. These views agree in ascribing the changes of reactivity to a drift of the electrons from their normal positions, not amounting to a complete transference. Now this electronic drift is exactly what the theory of resonance requires. To express the organic doctrines in terms of resonance we have only to imagine the drift extended to the point where a new structural formula is reached. This gives us the second resonance structure, and the actual state of the molecule is somewhere between the two.

I cannot discuss this in detail, but I may give one example where the evidence is peculiarly complete. In chlorobenzene (I) it is assumed by the organic theorists, to

* For references see *Ann. Reports*, **1934**, **31**, 38.

account for the ortho- and para-substitution, that there is a drift of electrons from the chlorine atom towards the ring (II). If we suppose this drift to go to the limit, we get a new formula (III; the two ways of writing it, III*a* and III*b*, mean the same thing); by a further change of the same kind the negative charge is transferred from the ortho- to the para-carbon atom (IV*a*, IV*b*). The properties implied by (II) are exactly those of



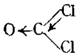
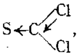
(I.) (II.) (III*a*.) (III*b*.) (IV*a*.) (IV*b*.)

a resonance hybrid of the structures (I) and (III). Physical evidence of two kinds has been obtained in support of this view. It has been shown by Sutton (*Proc. Roy. Soc.*, 1931, **133**, 668) that the dipole moment of chlorobenzene is less than that of a chloroparaffin, and so indicates an electronic drift towards the ring: he showed that wherever a substituent causes a drift in this direction it gives ortho- and para-substitution. The difference of moment in chlorobenzene is 0·6 D., which is about a tenth of what we should get by the complete transference of an electron from one atom to the next, so that the state of the hybrid must lie nearer to (I), and (III) must be the less stable form, which is what any organic chemist would expect.

Further evidence of the existence of links of the type of C$\overleftarrow{=}$Cl has been obtained by the measurement (by electron diffraction) of the X—Cl distances in a variety of chlorides. The radii of the atoms in question are already known from other compounds in which resonance does not occur; if there is resonance in any of these compounds, it should be shown by the X—Cl distance being less than the sum of the normal radii of X and chlorine. The distances in the tetrachlorides of carbon, silicon, germanium, and tin were measured by Brockway (*J. Amer. Chem. Soc.*, 1935, **57**, 958). He finds that the distance in carbon tetrachloride is what we should expect, but in all the other compounds is markedly less:

X—Cl	CCl_4.	$SiCl_4$.	$GeCl_4$.	$SnCl_4$.	$O{=}CCl_2$	$S{=}CCl_2$.
Calc.	1·76	2·16	2·21	2·39	1·76	1·76
Obs.	1·76	2·02	2·10	2·29	1·68	1·70
Diff.	±0	−0·14	−0·11	−0·10	−0·08	−0·06

Now resonance with the form $Cl_3X\overleftarrow{=}Cl$ is not possible with carbon tetrachloride, because the carbon atom cannot hold more than 8 electrons, but it can happen with the tetrahalides of silicon, germanium, and tin, which are not limited in this way, and the results show that it does so. Strong evidence in favour of this view is afforded by the measurements of Brockway, Pauling, and Beach (*J. Amer. Chem. Soc.*, 1935, **57**, 2704) of the C—Cl distance in carbonyl chloride and thiocarbonyl chloride. Here the resonance is possible without contravention of the covalency rule, since the carbon still has the

octet in the structures  and , and accordingly we find that the link is

shortened, as the above table shows. A further confirmation is given by the measurements of Brockway and F. T. Wall (*ibid.*, 1934, **56**, 2373) of the X—F distances in the hexafluorides of sulphur, selenium, and tellurium. The covalency limit for sulphur and selenium is 6, and for tellurium 8, so that only the last of these compounds can resonate. The calculated values here are not to be expected to agree with the observed for any of these compounds, because we have to use the radii of the dicovalent atoms; but we find a much larger difference with the tellurium compound than with the others. The figures are:

X—F	SF_6.	SeF_6.	TeF_6.
Calc.	1·68	1·81	2·01
Obs.	1·58	1·70	1·84
Diff.	−0·10	−0·11	−0·17

Those few examples will serve to illustrate the importance of the resonance theory, which has certainly come to stay, and which may be expected, in conjunction with the views of the organic theorists, to extend enormously our ideas of structural chemistry, and of its relation to reactivity.

I hope I have said enough to show that the modern development of the structural theory, far from destroying the older doctrine, has given it a longer and a fuller life; and further that the tendency of modern research is not to contract the scope of its material, but on the contrary to call in to its assistance an increasingly wide range of properties, and to bring to bear on its problems the results of every kind of physical and chemical investigation.

OBITUARY NOTICES.

HARRY BAKER.

1859—1935.

HARRY BAKER passed away on November 17th, 1935, at his home, Grange Court, Leominster, in his 77th year : his remains rest in the Friends Burial Ground. He was born in Bethnal Green in 1859, the eldest son of Henry Baker and Elizabeth Wright. In 1868 the family moved to Manchester, where Baker was educated at the Manchester Mechanics Institution, and from 1875 at Owens College where in 1878 he was elected Dalton Scholar for an original investigation on the fluorides of vanadium. In 1879 he studied inorganic chemistry under Professor Bunsen at Heidelberg University, also under Professor H. Kopp and Professor H. Rosenbusch. In 1881 he was elected to the Berkeley Fellowship in Chemistry at Manchester, giving special lectures on crystallography, being at the same time private assistant to Professor Sir Henry Roscoe. He was appointed Assistant Lecturer and Demonstrator in Chemistry at Owens College in 1882 and occupied this post until 1888.

The results of his work were published between 1878 and 1888 in the *Memoirs* of the Manchester Literary and Philosophical Society, the *Journal* of the Chemical Society, and Liebig's *Annalen*. His skill as a manipulator was remarkable and he possessed keen powers of observation, attributes which afterwards contributed to his successful work in industry.

The chemical industry claimed him in 1888 when he was appointed chemist to the Aluminium Company, Oldbury, nr. Birmingham, where he began his association with Hamilton Young Castner. He was to remain associated with Sir Henry Roscoe, who was a Director of the Aluminium Company. The Company was formed to work the aluminium process of Castner, who had come over from the United States, being unable to interest commercial men in that country in his new process for the reduction of aluminium chloride with sodium. After a few years this process, though technically successful, could not compete with the electrolytic production of the metal by Hall's process. Castner then turned to electrolytic processes and Baker assisted him in developing the cell for the production of sodium in 1890. In 1891 a process for producing sodium peroxide was devised. In 1892—1894 the Castner rocking cell was evolved for the production of chlorine and pure caustic soda, a soda of high purity being necessary for the electrolytic sodium process. In 1894 a process for producing sodium cyanide was perfected; this process was the basis of the highly successful Cassel Cyanide Company and was transferred to Glasgow on the death of Castner, Baker having by then been appointed chief chemist to the Castner Kellner Company, whose works at Runcorn subsequently became the largest chlorine-producing factory in the world. The process for producing graphite electrodes was evolved in 1896, but was developed by Acheson at Niagara, where ample electric power was available. Baker visited the States, Germany, and Austria in connexion with the installation in those countries of Castner's processes. His pioneer work in collaboration with Castner was necessarily unknown to the scientific world, but its value was immense and it is a tribute to the work of Castner and Baker that the electrolytic processes invented and perfected by them should hold such a prominent position in the chemical industry of to-day. As a colleague both at the University and in industry he inspired affection and his example as a leader was always a stimulus to those who had the good fortune to work under him.

Mary Eccles, whom he married in 1889, survives him. His two sons carry on the scientific tradition, Henry being Lecturer in Engineering at Manchester University and Wilson being Lecturer and Demonstrator in Chemistry in the Dyson Perrins Laboratory, Oxford. His daughters, Margaret and Mary, have achieved distinction as writers and illustrators of children's books.

E. OTHO GLOVER.

KENDALL COLIN BROWNING.

1875—1936.

Kendall Colin Browning was born at Wimbledon in 1875, the second of three sons of the late Staff Captain G. A. Browning, R.N., and Mary, daughter of Dr. Kendall of King's Lynn. He was educated at Dulwich College, where he studied chemistry under H. Brereton Baker, and gained a leaving scholarship to St. John's College, Cambridge, of which he was senior foundation scholar. At Cambridge his work was originally directed towards obtaining a medical qualification, but he finally decided to take chemistry as his principal subject. In 1896 he obtained a First in Part I of the Natural Science Tripos, his subjects being Chemistry, Physics, Physiology, and Mineralogy, and graduated B.A. in 1897 with a First in Chemistry and Physics in Part II of the same tripos. In this year he was Hughes prizeman, and was appointed demonstrator and assistant lecturer under Adie, occupying this post for three years. In 1899 he was also supervisor of medical students. In 1898 he was awarded a Hutchinson research studentship, which he held for two years, taking his M.A. in 1900.

He rowed for his College, was awarded a half blue for cycling, and was a Captain in the University Volunteers. In his post-graduate period he worked under Ruhemann and Adie, the results of their joint work being published in the *Journal* of the Chemical Society and in the *Berichte*.

In 1904 he was appointed Professor of Chemistry at the Medical College (now University College), Colombo, and public analyst for Ceylon. Owing to pressure of work he relinquished his teaching duties in 1907, and in 1910 he became head of the newly formed Government analysts department. Here his work was of a very varied nature, consisting largely of criminological investigations, in which his early medical training proved of great value, and of work for the Customs, Excise, and public health authorities. He was also responsible for the drafting of a new Food and Drugs Act, which ultimately became law.

In 1916 Browning, having been recommended to the War Office by H. Brereton Baker to carry out special work in connexion with water supplies for the British troops in Mesopotamia, came home to England for preliminary military training. It was then that his health broke down, preventing him from taking up this work. In 1917 he was commissioned in the Royal Engineers, and seconded to the Ministry of Munitions, where he worked with Prof. T. M. Lowry, Technical Director of Gun Ammunition Filling, on problems connected with the high explosive and gas fillings of shell. He was a member of a special mission sent to France to carry out experiments on chemical warfare, and there contracted the bronchial trouble that finally caused his death.

At the end of the War, he was joint author, with Prof. T. M. Lowry and J. W. Farmery, of a paper on the decomposition of nitric esters by lime; this work originated in experiments carried out by the late Prof. W. R. E. Hodgkinson at the Ordnance College (now Military College of Science), Woolwich, and continued by the Waste Explosives Committee under the direction of Prof. T. M. Lowry, with the object of working out methods for usefully disposing of the enormous quantities of cordite and other explosives which were left at the conclusion of the War.

On demobilisation, Browning worked for a short time under his old teacher, H. Brereton Baker, at S. Kensington, and in 1921 he was appointed Professor of Chemistry and Metallurgy at the Artillery College (formerly Ordnance College and now Military College of Science), Woolwich. In the following years he made a special study of problems covering the properties of fuels and lubricants in their relations to the internal combustion engine.

As a teacher, Browning commnnicated his enthusiasm to his students, and possessed an encyclopædic knowledge of technical literature which was always at the disposal of those who were privileged to work under him. He had great strength of will, which enabled him to continue working in spite of great physical obstacles until within a few months of his death, which occurred very suddenly at Dawlish, on January 26th, in his sixty-first year.

R. C. Gale.

WILLIAM FREDERIC BUTCHER.

1867—1936.

W. F. Butcher was born in Woolwich, his father being a registered pharmacist in that town, and was educated at Margate College. Subsequently qualifying as a pharmacist, in 1889 he joined his father's business, which had then been moved to Blackheath.

Butcher was a man of great forcefulness of character, and quickly took a leading part in developing the wholesale side of the business. An enthusiastic amateur photographer, his activities were in a few years diverted to photography. He established a small camera factory, and was a pioneer in the wholesaleing of photographic apparatus and materials amongst retail chemists.

By 1903, the photographic and pharmaceutical aspects of the business were separated, and a private limited company formed with premises at Camera House, Farringdon Avenue, E.C. In 1915, with six of the principal photographic firms in London, he assisted in forming British Photographic Industries, Ltd., employing over 3,000 people. Butcher was Vice-Chairman of this Company: in 1926 the two principal companies, Houghton and Butcher's, were merged into Ensign, Ltd., at Holborn.

Notwithstanding his absorption in business affairs, Butcher found time for outdoor recreations, including golf, tennis, swimming, ski-ing and climbing, taking an active part in such sports until within six months of his death, which occurred on January 12th, 1936. He was much loved by a large circle of friends, and is survived by a daughter and two sons. He was elected a Fellow of the Chemical Society on December 5th, 1889.

Isidor Joseph.

HAROLD WARD DUDLEY.*

1887—1935.

By the untimely death of Harold Ward Dudley, before he had completed his 48th year, Science has lost a devoted servant and a distinguished investigator. The wide influence which he had acquired, especially among those concerned with biochemistry, was due to his fine character and his personal charm, as well as to his already distinguished record of research; and his services to the remarkable development of that branch of science in this country, apart from the direct effect of his own investigations, involved a quiet and unselfish devotion of time and work to the interests of his colleagues.

Dudley was born at Derby on October 30th, 1887, as the eldest son of the late Rev. Joshua Dudley, who, as a Methodist minister, was stationed for successive periods in different parts of the country. Harold Dudley's schooling changed with these movements of his home. He was at Truro College, and at the King Edward VI Grammar School, Morpeth, from which he entered Leeds University, taking chemistry as his subject, and specialising in organic chemistry. This brought him under the influence of the late J. B. Cohen, F.R.S., who died earlier in 1935. Cohen was not only a great and inspiring teacher; there must have been something in his teaching of organic chemistry which aroused interest in its biological significance, to account for the number of his pupils who have won success and distinction in biochemistry. It is sufficient to name, in order of seniority, Dakin, Raper, Hartley, Dudley, Woodman, Raistrick, and Wormall, to realise that the teaching of Cohen, himself no biologist, has had, through his pupils, a powerful influence on the development of this relatively young department of science. Dudley, after graduation in chemistry, began research under Cohen's guidance, and proceeded to the higher degree of M.Sc. with a contribution on "The Relation of Position Isomerism to Optical Activity in Certain Menthyl Esters." He was then awarded a Science Research Scholarship by the 1851 Commissioners, and, under Cohen's advice, went to Emil Fischer's famous institute in Berlin. There he worked with Professor Wilhelm Traube on the chemistry of the purines, and took the degree of Ph.D. in 1912.

* Adapted by Dr. H. King from the obituary notice by Sir Henry Dale in the *Proceedings* of the Royal Society.

When Dudley returned to England in 1912, there came to him an opportunity which had a decisive influence on his career. The late Dr. Christian Herter, of New York, had equipped the top floor of his house in Madison Avenue as a laboratory for research in medical and biological chemistry. H. D. Dakin, who had been invited by Herter to work in this private laboratory, had been engaged there since 1905 in fundamental researches in biochemistry, and remained in charge of the laboratory after Herter's early death in 1910. In 1912 he was seeking an assistant and collaborator, and through his old teacher Cohen was brought into touch with Dudley. The appointment was offered and accepted, and Dudley entered upon two years of happy, intimate, and fruitful collaboration with Dakin, who already had problems of great interest awaiting further development. These joint researches belong mainly to two groups. One group was concerned with the function of glyoxals in the metabolism of carbohydrates, and in the intermediary metabolism of carbohydrates and amino-acids. In this connexion Dakin and Dudley discovered the tissue enzyme glyoxalase, and devised a method of measuring its activity by following the conversion of phenylglyoxal into mandelic acid.

The other group was concerned with the partial racemisation of proteins by treatment with warm alkali. When the constituent amino-acids were separated from such racemised proteins by acid hydrolysis, it was found that only some of them had undergone racemisation, and theoretical grounds were given for the views that these were the terminal members of the peptide chains from which the complex molecules were built. A further observation of great interest was that a protein which had been thus treated, until the racemisation process had reached its end point, was completely refractory to digestion by proteolytic enzymes, and behaved in the body like an inert substance, passing rapidly through the kidney into the urine. Experiments made by Ten Broek showed that it had completely lost its antigenic properties.

Dudley's two years in New York had given him a wealth of experience and of ideas, in the subject which was now to be his life's work. He had made many pleasant personal contacts in scientific circles in America; and he had formed an intimate and lasting friendship with Dakin, and with Mrs. Herter (now Mrs. Dakin) and her family. He was ripe for independent activity when he returned to Leeds, in 1914, as Lecturer in Biochemistry in the Animal Nutrition Research Institute. Here he was quickly engaged with problems arising from his work with Dakin, as shown by papers, published in 1915, on the estimation of glyoxalase in blood, and, jointly with H. E. Woodman, on the caseins of cow's and sheep's milk. No difference could be found between these two proteins, as regards the nature of the amino-acids constituting them or the proportions in which these were present. Application of the racemisation method, however, revealed a clear difference between the amino-acids which became racemised in the two cases, indicating a specific difference between patterns of their linkage in the respective molecules.

The outbreak of war soon terminated Dudley's work at Leeds. He obtained a commission in the army, and was detailed for special work on protection against the new chemical weapons of war, which he performed with characteristic thoroughness under the late Professor Starling, and subsequently under the late Brigadier-General Harrison, at the R.A.M. College at Millbank. Early in 1918, having been promoted to the rank of major, he was sent to the United States of America, where his thorough knowledge of the British experience, his acquaintance with American conditions, and his many personal contacts in that country specially qualified him for an advisory mission to the new anti-gas organisation of the American army and its mechanism of supply.

When the end of the war came, Dudley, whose services were recognised by the award of the O.B.E., was ready and eager to return to his normal activity in research. I was reorganising the Department of Biochemistry and Pharmacology under the Medical Research Council, in preparation for its transfer from war-time quarters in the Lister Institute to its permanent home in the National Institute for Medical Research at Hampstead, which had been occupied throughout the war as a military hospital. My first colleague in the department, George Barger, had already left to take the new Chair of Medical Chemistry in Edinburgh. The needs of the future suggested the appointment of two younger men, one to be concerned mainly with biochemistry in the stricter sense and the

other with the chemistry of drugs and synthetic remedies. I was fortunate in finding Dudley and Harold King ready to accept appointment, and they joined our team together. There was much planning and organisation to be done, in converting rooms which had originally been hospital wards, and in use as such until well into 1919, into experimental laboratories. The most extensive adaptation and installation was required in the case of the chemical laboratories, and for this Dudley, with King's co-operation, made himself responsible. In later years the equipment was much extended and included a laboratory for extracting and concentrating materials on a semi-manufacturing scale, for which Dudley, again, took the chief responsibility.

While the initial minimum of equipment was being installed, up to the spring of 1920, research went on in our temporary quarters, and here Dudley carried out an important part of his work on the hormones of the pituitary posterior lobe. It had long been known that an extract from this organ had powerful stimulant effects on the muscular walls of the arteries and on that of the uterus. These had generally been regarded as two expressions of the activity of one principle. When Dudley, at my request, undertook investigations on its chemical properties, and applied a method, then newly introduced by Dakin, for the separation of amino-acids, in which the watery solution was continuously extracted by butyl alcohol, the substance acting on the uterus was completely extracted, while the pressor principle remained largely in the watery residue. The presence in this extract of two different substances, each responsible for one only of its principal activities, was for the first time made clear. The discovery was not unchallenged, and Dudley was involved with me in further work, some of it giving further information of interest, some of it disappointing; but no published item of Dudley's contribution has to my knowledge needed revision. By methods later found by Kamm and others, the two principles in the extract are now separated on a large scale, and offered in separate solutions for practical use in therapeutics; so the correctness of Dudley's original observation is no longer in question.

During 1922 private information came from Toronto to the Medical Research Council of the rapid development of Banting and Best's discovery that the antidiabetic hormone, insulin, could be obtained by artificial extraction from the pancreas. The Council were invited to send scientific observers to report to them on the progress of this remarkable discovery, and the initial results of its practical application. I was asked to undertake this mission of enquiry, and, at my request, Dudley was sent with me. We arrived at Toronto towards the end of September, 1922, and the evidence put before us carried immediate conviction that a genuine discovery of great potential importance had been made. The late Professor J. J. R. Macleod had organised a team of workers to reinforce the activities of the original discoverers, in work directed to the improvement of methods for estimating the amount of insulin present in extracts, and to the production of purer preparations in a higher yield. The practical production was, indeed, still in its infancy. The Toronto laboratory was working feverishly, with makeshift apparatus installed in a cellar, to keep pace with the demand for insulin for the continued treatment of a few cases already receiving it. Dudley and I visited also the factory of Eli Lilly & Co., at Indianapolis, who had already, with much larger facilities, been co-operating with the Toronto workers in the effort to arrive at a large-scale production of insulin in a suitably pure solution for therapeutic use. Though there was a clear promise of improvement with experience, there was no certainty as to its extent at the time of our visit. A yield of 5 " units " of insulin from a kilogram of pancreas was still regarded as a good result; and the extract containing it was highly impure, of poor stability, and liable to lose a large part of its insulin during passage through a sterilising filter. On our return, Dudley worked, with his usual quiet efficiency, to find a process which could enable manufacturers to produce insulin on a scale and at a price which would bring it within the reach of all who needed it. He found that the conditions for its successful extraction did not depend, as had been supposed, on protecting it from trypsin, but on a reaction sufficiently far, on either side, from the isoelectric point of the hormone; he found that loss in filtration could be eliminated by adjustment of the reaction to an appropriate acidity; and he discovered a method by separation as a picrate and reconversion into a hydrochloride, of purifying crude insulin and obtaining it in a dry stable condition. Within a few months he could give to the manufacturers a process

yielding 500 instead of 5 units of insulin from a kilogram of the raw gland. I do not know to what extent these discoveries of Dudley have survived in modern manufacture. It is certain that others as important were concurrently being made in Canada and America. What is also quite certain, however, is that British manufacture was enabled, by his devoted and concentrated activity, rapidly to overtake the effort on the other side of the Atlantic, so that the solution of the practical problem was in sight as early in this country as in any in the world. When, in 1923, an International Conference decided to adopt a stable standard preparation of insulin for world-wide use, and to define the unit in terms of it, Dudley was charged with the preparation of this first insulin standard.

Dudley now became interested in an entirely different problem. Otto Rosenheim, who had worked with Mrs. Rosenheim many years earlier on the curious base spermine, widely distributed in the tissues and still of unknown function, made contact with the Institute and with Dudley, at a time when the demands of the insulin work were becoming less urgent. They embarked on a co-operative investigation which, with remarkable rapidity, led to the extraction of spermine on a scale enabling them to determine its curious and unexpected constitution—$\alpha\delta$-bis-(γ'-aminopropylamino)butane—and to confirm this by synthesis. A second base, spermidine, which accompanied spermine in tissues in smaller quantity was proved by analysis and synthesis to be α-(γ'-aminopropylamino)-δ-aminobutane.

For many years I had been interested, with a succession of colleagues, in the action of the base histamine, with its remarkably faithful reproduction of a syndrome occurring in various physiological and pathological reactions, and also caused by the injection of extracts from many animal organs and tissues. A second visit of C. H. Best to my laboratory, primarily for further investigation of a liver extract showing this general type of action, led to the association of Dudley and W. V. Thorpe, who had recently joined him, with Best and myself, in an effort to determine the relation between histamine and the substances causing this action. The chemical side of the work, which was Dudley's direct responsibility, led to the isolation of histamine itself, with relatively large amounts of choline, from the liver extract. The investigation was extended to the lung, in extracts from which we had been able to demonstrate a very pure and potent activity of the histamine type, and again histamine was obtained by Dudley and Thorpe, in a yield sufficient to account for all the activity of this type, and under conditions which precluded post-mortem development or artificial production by the chemical procedures used in its isolation. For the first time we had evidence that this powerful base is a normal constituent of the living cells, and the evidence was extended to other tissues by Thorpe, working by Dudley's methods and with his advice.

One organ had been omitted from this survey of the tissues for histamine, namely, the spleen. When Dudley and I proceeded to fill this gap, he obtained the histamine without difficulty from extracts of the spleens of oxen and horses, by the methods which he had already used with other tissues. We were early met, however, by evidence of an intense action of the choline type, disappearing very readily if the extract was made alkaline and left to stand. The presence of an unstable choline ester in these spleen extracts seemed to be indicated, and it was natural to think of the interesting possibility that it might be acetylcholine. Its great instability made the attempt to separate it from the extract, with the methods then available, a rather uncertain enterprise. Dudley tackled the problem with his usual quiet efficiency, and in due course isolated acetylcholine as the gold and platinum salts in quantities sufficient for complete chemical identification; so that acetylcholine, the possible occurrence of which in the body was the subject of much speculative physiological interest, was demonstrated, beyond question, to be a natural constituent of an animal organ. Incidentally to this investigation, Dudley observed that the chloroplatinate which crystallises easily from solutions containing both choline and acetylcholine is not, as had been supposed, the chloroplatinate of acetylcholine, but a double salt of both bases. He also devised a characteristically elegant method of recovering delicate and unstable bases from their gold and platinum salts, in the form of their neutral hydrochlorides, by the addition of metallic silver.

This discovery of acetylcholine in the animal body, with its physiological implications,

aroused wide interest. It was not long before claims were put forward, from a continental laboratory, for the isolation of acetylcholine, in some cases in very large quantities, from practically every organ of the body. Dudley and I eagerly took up the question again, but, at the cost of much fruitless labour, he found himself entirely unable to confirm these findings. The mystery was only deepened when he visited the laboratory of their origin, confirmed them there, and again consistently failed to reproduce them by exactly the same methods in his own. His gentle nature disliked and shrank from controversy; and, even by those who would regard tbe scientific point at issue as still undecided, I believe that his statement of his observations under these different conditions would be accepted as perfect in its courtesy and its quiet candour.

The last research which Dudley brought to the point of publication was that which resulted in the isolation and description of a new alkaloid from ergot, "ergometrine," the properties of which indicate that it is likely to be accepted as the essential active principle of that remarkable drug, in relation to its principal and traditional use in obstetrics and gynæcology. The clinical experiments of Chassar Moir had given clear evidence of the existence, in watery extracts of ergot, of a substance having a very prompt and powerful stimulant action on the uterus when administered by the mouth. This did not correspond with any of the alkaloids or other active substances which ergot had hitherto yielded; and Dudley, in 1932, embarked upon an attempt to isolate the substance responsible for this action, with the close co-operation of Chassar Moir, who submitted Dudley's preparations to a clinical test at every stage. Various circumstances delayed progress, and by the time Dudley had the alkaloid in his hands, with clear evidence that it was the substance for which they were seeking, workers in other centres were hot on the trail. His publication in March, 1935, in which he gave a preliminary description of the alkaloid and named it ergometrine, was quickly followed by other claims to its discovery and to the right to name it. The discovery and its sequel came at a time when Dudley was suffering from the deepest of personal tragedies. Marred though it was by his dread of controversy, the refuge from sorrow which he found in the interest of his new discovery, and in the work still needed to bring it to his own high standard of perfection, enabled him to keep his outward placidity and to finish what he had in hand. His completed description of ergometrine was sent for publication shortly before his fatal illness, and was published in the *Proceedings* of the Royal Society on October 3rd, the day of his death.

Apart from his services to biochemistry through his own researches, Dudley did a great deal of quiet and effective work for his colleagues in that branch of science, as Secretary of the Biochemical Society (1922—1924), as co-editor, with Sir Arthur Harden, of the Biochemical Journal (1924—1930), and as editor of the biochemical section of Chemical Abstracts for the Chemical Society. He was elected F.R.S. in 1930.

Ever ready to spend his time and his knowledge in helping others, Dudley was an ideal collaborator. Inspection of a list of the writings to which his name is attached, will show how preponderantly he worked with others. In some cases he worked with junior colleagues, who found him an effective and encouraging teacher and leader. A good deal, however, ever in his maturity, was done with senior co-workers. I think it would be true to say that Dudley, sure of his technique and always interested in finding methods for tackling problems which had baffled others, was diffident of his own initiative, and worked more happily and with greater confidence when others had taken the responsibility of suggesting a main objective.

Even those who did not know Dudley personally might have been able to form a partial, but not inaccurate, conception of the man from his work. There was a modest elegance and a feeling for perfection in all that he did, which matched with, and indeed formed part of a fine character and personality. Tall and graceful, with a ready and charming smile, Dudley was shy of pretention, of volubility, of exaggeration of any kind, and of any display of emotion. He found his recreation in the gentle sport of fly-fishing. I do not remember to have seen him show anger; a half-humorous annoyance was normally his nearest approach to it. Yet his friends knew that he was a man of very deep feeling, and of warm and loyal affections. His marriage to Miss Mary Nettleship in 1921 brought him great happiness, though the shadow of a coming tragedy was early cast by her illness in 1922.

In the years that followed, her frequent failures of health were faced with a buoyant courage, and a perfect devotion to one another. Her death in April, 1935, after a long illness, plunged Dudley into a grief which he could not share; but the bravely hidden sorrow had left him too little reserve to meet his own illness, entailing a serious operation, six months later.

H. H. DALE.

CHARLES RICHMOND FEATHERSTONE.

1885—1936.

CHARLES RICHMOND FEATHERSTONE, who died on January 23rd, 1936, was born in 1885 at Bishop Auckland. He was educated at the Grammar School, Stockton-on-Tees, and won an open scholarship in Natural Science to Lincoln College, Oxford, where he obtained an Honours Degree in chemistry in 1908.

His first post on leaving Oxford was at Greenock Academy and from there he went as Second Science Master to King Edward's Grammar School, Aston, Birmingham, becoming Senior Science Master the following year.

He was appointed Senior Science Master at St. Peter's School, York, in 1915, where he remained until his death. He became House Master of Clifton Rise in 1918.

At St. Peter's he reorganised the Science side, introducing improvements in the laboratories, starting a course in biology in 1922, and giving to the school a well-designed post-certificate course in science.

One of the features of which he was justly proud was the Scientific Society which he founded and led with great wisdom until it became a strong influence amongst the boys. His underlying motive was to make the Science side useful to all the boys and not merely to the specialists, by discovering and fostering their native interests. Almost my last recollection of him was as we walked round the Members' Exhibition at the Science Masters' Association in London a week or two before he died, taking notes of what he saw and murmuring " That's good—the boys will appreciate this."

He was a science teacher of considerable inspiration, combining an intense love of his subject with a breadth of view quite unusual, and with a meticulous care in preparation. He read widely and gave freely of his time and energy to all who came under his care. His study in his House was a haven for boy or colleague, and all he possessed was freely at their disposal. With great courage he bore an affliction which precluded him from active participation in school games, but he never failed, by his presence and encouragement, to demonstrate his interest in all school activities.

He was one of the older members of the S.M.A. and was one of the Committee of the young branch of that Association in Yorkshire. He was for many years a keen member of the York and District Field Naturalists' Society, being their President in 1928, taking as the subject of his Presidential address, " Plant Life in the Past." The members of that Society " remember him gratefully for the unassumiug and friendly way in which he was always willing to place his services at their disposal." One of his great interests was the study of trees, but in addition he was a student of geology and astronomy. At the last meeting of the British Association in York, 1932, he was the local Secretary for the Mathematical and Physical Section.

Of no man could it be more truly said that " his work was his hobby." His first and last thoughts were for his boys. He attracted and held others by his obvious sincerity; his gentleness was not softness, but carried with it the austerity of conviction. He was modest of demeanour, upright in character, generous in thought and word, kindly considerate of others; he was respected by all and beloved by those who were privileged to know him intimately.

Thus has passed a loyal and devoted servant of his age who was not without reward during his lifetime in the affection he inspired, just as he himself never failed to pay tribute to the inspiration and influence on his life of the present President of the Chemical Society.

He was a keen Churchman and it is fitting that an oft-expressed wish to see the Sanctuary in the School Chapel panelled should be fulfilled as a memorial to him.

C. E. L. LIVESEY.

GEORGE ALECK CROCKER GOUGH.

1902—1935.

GEORGE ALECK CROCKER GOUGH, born on April 23rd, 1902, was educated at Battersea Secondary School from 1917 to 1919 and at Battersea Polytechnic from 1919 to 1926. He was a brilliant student and in 1922 took the degree of B.Sc. (Lond.) with first-class honours in chemistry and in 1925 was awarded the degree of Ph.D. for a contribution to the stereochemistry of the methyl*cyclo*hexanols (J., 1926, 2052). Gough was a product of the remarkable school of chemistry at Battersea represented by Pickard, Kenyon, Hunter, and Phillips at the zenith of its activity.

In September, 1926, Gough joined the author on the staff of the chemical laboratory at the National Institute for Medical Research at Hampstead. I soon discovered that he had a remarkable aptitude for experiment, which received full play in the difficult unexplored field of amphoteric aliphatic arsonic acids (J., 1928, 2426) and again in aromatic acids containing amide groups (J., 1930, 669). A laboratory bench with half a dozen operations proceeding at once was characteristic of Gough. During the last-named investigation the preparation of nicotinic acid was undertaken and this led to the strange discovery of a nitropyridylpyrazole as an oxidation product of nicotine (J., 1931, 2968; 1933, 350).

In 1929 Gough was awarded a Rockefeller Travelling Fellowship for research in biochemistry. Full of enthusiasm he proceeded to Münich, where for a year he worked in Wieland's laboratory on some subsidiary sterols of yeast (*Annalen*, 1930, **482**, 36). On the completion of his studies in Münich he proceeded to Graz, where he took a course of microchemical analysis under Pregl.

On his return to Hampstead, Gough took up the chemistry of bacterial products. A great fillip had been given to bacterial chemistry by the work of Heidelberger and his colleagues on the isolation of complex specific polysaccharides from cultures of various types of pneumococci and it was a possibility that similar progress could be made with tubercle bacilli. Just at this time R. J. Anderson in the United States was embarking on an examination of the fats and waxes of tubercle bacilli, and Gough, on the suggestion of the late Dr. H. W. Dudley, took up the complementary investigation of the carbohydrates and proteins.

From tubercle bacilli grown on a synthetic medium, a specific carbohydrate, with a precipitating power against immune serum at a dilution of 1 in 5 millions, was isolated. On gentle hydrolysis it yielded mannose, *d*-arabinose, galactose, and an acidic fraction which on more prolonged hydrolysis gave more mannose (*Biochem. J.*, 1932, **26**, 248). Incidentally an investigation was made of the polysaccharide fraction isolated from the pollen of Timothy grass (*Phleum pratense*), since pollen are known to be associated with allergic conditions in man. This polysaccharide displayed some similarity to the specific carbohydrate of the tubercle bacillus and on hydrolysis gave *l*-arabinose, galactose, and a non-reducing acid (*ibid.*, p. 1291). Then followed a research into the water-soluble proteins of tubercle bacilli, whereby an albumin and a globulin were isolated, without denaturation, showing different chemical and immunological properties (*ibid.*, 1933, **27**, 1049).

It was but natural that the tubercular diagnostic agent tuberculin should be examined, and Gough showed how a highly active tuberculin could be obtained from a fresh culture medium by adsorption on benzoic acid. Such a tuberculin consisted essentially of large protein molecules, but from an old tuberculin two different fractions of widely differing molecular size were prepared, both, however, possessing skin activity (*Brit. J. Exp. Path.*, 1934, **15**, 237).

Gough's last contribution to chemical bacteriology was in collaboration with Dr. F. M. Burnet, on the chemical nature of the bacteriophage-inactivating agent in bacterial extracts.

This substance was polysaccharide in nature and on graded chemical treatment it lost in a step-wise fashion its ability to inactivate different phages (*J. Path. Bact.*, **1934**, **38**, **301**).

Gough was elected a Fellow of the Chemical Society in 1926 and an Associate of the Institute of Chemistry in 1924. He was a member of the Biochemical Society and of the Microchemical Club. For three winter sessions he gave an evening course in microchemical methods at the Sir John Cass Technical Institute. Late in 1934 Gough developed a mysterious illness, which ended fatally on November 8th, 1935. He was laid to rest in beautiful surroundings among the magnificent wych-elms in the grounds of the old parish church at Ashtead.

Gough had a strong affection for his garden and for the beautiful woodlands and commons of his native Surrey and for their fauna. He was keenly interested in art-photography, and was a skilled glass-worker. On chemical matters I invariably found him a sound critic, and all laboratory hypotheses in their embryonic or mature stages were tried on Gough with beneficial results. Calm, patient and unperturbed, Gough pursued his daily round with a devotion to duty only exceeded by his attachment to his widowed mother, who survives him.

HAROLD KING.

MAX HENIUS.

1859—1935.

MAX HENIUS, who was well known in both Denmark and the United States of America, was born at Aalborg, Jutland, where he received his early education. His training in chemistry was at the Polytechnic High School, Hanover, and the University of Marburg, where he graduated Ph.D. in 1881. In the same year he emigrated to the United States, where he and Dr. Robert Wahl in 1886 established the firm of Wahl and Henius, analytical and consulting chemists, at Chicago. The Wahl-Henius Institute, which included the American brewing school, came into being in 1891, Dr. Henius being director and later President.

His publications were limited mainly to articles on fermentation and its technology, patents in connection with brewing, its plant and equipment, and in particular, he and his partner were co-authors of the well-known text book, "Wahl-Henius Handy Book of the Brewing, Malting and Auxiliary Trades." He also wrote a number of pamphlets during 1931—34 advocating temperance (in the strict meaning of that word), such as "Modern Liquor Legislation in Finland, Norway, Denmark and Sweden."

Henius frequently served in such capacities as delegate, secretary or judge at various international congresses and exhibitions associated with the fermentation industries. He was a member of many British Societies, including the Chemical Society. Outside his professional activities, he did much to establish good relations between the countries of his birth and adoption, particular examples being in connection with the Rebild National Park in Denmark, which was provided by Americans of Danish descent, and an American Reference Library at Aalborg. Denmark honoured him by making him a Knight of the Order of Dannebrog, and awarding him the Gold Medal of Merit.

The outstanding feature of the life work of Henius is, however, that he was conspicuous as a pioneer of science in an industry which was an empirical handicraft in America when he first came into association with it.

R. H. HOPKINS.

FRANCIS RANSOM.

1859—1935.

FRANCIS RANSOM, the only son of William Ransom, was born at Fairfield (now known as Little Benslow Hills) on May 18th, 1859. In 1882 he entered the School of the Pharmaceutical Society, and after passing the Minor and Major Examinations continued as a

research student under Professor W. R. Dunstan (now Sir Wyndham Dunstan). He carried out researches on belladonna and published several papers in the *Pharmaceutical Journal*. After leaving the School, he gained experience in the works of Messrs. Southall Bros. and Barclay, and at Queen's Hospital, Birmingham. In 1884, he became a partner in the firm of Messrs. William Ransom and Son, at Hitchin, widely known for the cultivation of medicinal plants and the distillation of essential oils, and on its formation as a private limited company in 1913, was elected Chairman of the Board, a position he held until his death.

From 1886, for nearly 12 years, Ransom served on the Board of Examiners of the Pharmaceutical Society; he was Honorary Secretary of the Pharmaceutical Conference from 1890 to 1903 and President of the Conference held at Cambridge in 1910. As a result of his generosity, in 1916, the Ransom Fellowship for research in pharmacy was founded by the Pharmaceutical Society for the purpose of promoting work in the investigation of crude drugs and the solution of problems having a purely pharmaceutical bearing.

A man of great business acumen, Ransom had wide interests and devoted much time to public service in Hitchin. He was a vice-president of the local hospital, a member of the Hitchin Guardians for many years and chairman from 1926 until ill-health rendered his retirement necessary in 1930. He also had many other interests in the town, and was a Justice of the Peace for Hertfordshire.

For him pharmacy had pride of place and in the manufacture of its finer products he met the demands as they arose for improved appliances and experimental technique. His knowledge of crude drugs and their adulterants was wide and exact and extended to their assay where chemical methods were applicable, and to the isolation of their active principles. As a landowner he allocated an extensive acreage to the growing of plants that long have received official recognition by their inclusion in British and foreign Pharmacopœias, notably those of belladonna, henbane, digitalis, chamomile, and peppermint.

His recreative hobbies were the collection of prints and etchings, and especially of Japanese knife handles, of which his cabinet included some of the finest specimens to be found in this country. Of philately he made a life-long and careful study and was an unwearied enthusiast; his select and costly collection contained many stamps of exceptionally great value and variety. Out of his abundance he gave freely, cheerfully, and discriminatingly, and he generously supported local charities, in most cases anonymously. By temperament he was shy and retiring, as modest as he was capable, and to his intimates charming.

His death on December 19th, 1935, was a severe loss to British pharmacy, and at Hitchin he will ever be remembered with gratitude by his fellow citizens.

He was elected a Fellow of the Chemical Society on May 16th, 1889.

W. A. H. Naylor.

WILLIAM CHARLES YOUNG.

1849—1935.

William Charles Young, born in 1849, at Peckham, then a pleasant suburb of London, died at Ealing 11th October last, aged 86 years.

Young received his early scientific education from G. B. Buckton, F.R.S., and at the Royal College of Chemistry, where he became lecture assistant to Hofmann, and assisted Bunsen in his lectures delivered at the College. Then he worked under Mathiessen at St. Mary's Hospital on the zinc ethyl synthesis, followed by three years as assistant and demonstrator under Odling at St. Bartholomew's Hospital.

On Odling's appointment to the Waynflete Chair at Oxford, Young went to Attfield at the Pharmaceutical Society as his chief assistant, and then to Heisch, Middlesex Hospital, in the same capacity for three years.

At this point, attracted to the new field of work which recent legislation for the public health had opened for professional chemists in controlling the quality of food, drugs, water and coal gas, Young abandoned academic chemistry as a professional career and started practice in the year 1871, as analyst and consultant. His first official appointment, as Gas

Examiner at Beckton, jointly for the Corporation of London and the Metropolitan Board of Works, was followed by those of Public Analyst for the Poplar, Whitechapel, St. George-in-the-East, West Ham and other municipal areas, Consulting Chemist to the River Lee Conservancy (in which capacity he served for more than fifty years), Official Gas Examiner for West Ham, Leyton, Woolwich, Northfleet, Hastings, Littlehampton, Bognor, and for several other local authorities.

Young had for many years a wide and diverse private practice as consultant and adviser in the gas industry and in sewage and water pollution questions. Nevertheless, he made time concurrently for research, chiefly directed to improvement in analytical methods, of which records are to be found in the contemporary journals.

He was a Fellow of the Chemical Society (1873), the Institute of Chemistry (1878), the Society of Public Analysts, the Society of Chemical Industry (founder member), and the Imperial Institute.

W. M. GATHORNE YOUNG.

SAMUEL COX HOOKER.*

1864—1935.

THE death of Dr. Samuel Cox Hooker at his home in Brooklyn, N.Y., on October 12th, 1935, removed from the ranks of American chemists one of its most remarkable figures. He was born on April 19th, 1864, at Brenchley, in the County of Kent, England. His father, John Marshall Hooker, an architect, was the son of Stephen Hooker, a country gentleman, who, like his immediate ancestors for several generations, had lived and died at Brenchley. The family tombs in and outside Brenchley Parish Church record much family history. His mother was Ellen Cox, daughter of Samuel Cox of St. Heliers, Jersey, and also of Demerara, British Guiana, where he owned sugar plantations.

Shortly after Hooker's birth his parents moved to South Kent, and then after a brief interval to Sevenoaks. It was here that he spent most of his childhood and received his preliminary education, chiefly at Queen Elizabeth's Grammar School. At the age of 17 he was at the head of his classes.

In early boyhood Hooker became much interested in photography at a time when the wet collodion process was in general use. In this, and the succeeding period, when dry plates were being iutroduced, Hooker kept in close touch with developments in the art. He prepared his own plates and evinced that same mastery of detail and resourcefulness which characterised all his later work in chemistry and technology. The operations involved in these photographic pursuits naturally turned the boy's attention to chemistry, and so it came about that young Hooker in 1881 entered the Government Science School at South Kensington, London, of which Professor Huxley was then the head. He made rapid progress in his scientific studies and after two years was awarded a prize for advanced scholarship in chemistry. During this period he worked with Professor F. R. Japp, and the article by Japp and Hooker "On the Action of Aldehydes and Ammonia on Benzil" (J., 1884, **45**, 672) marks the first appearance of the junior author's name in chemical literature. This paper, published when Hooker was only 20 years of age, gave promise of future attainments in the field of organic chemistry.

In 1884 young Hooker left London to continue his chemical studies at Munich, where he worked under Bamberger in continuation of the latter's investigations upon retene, $C_{18}H_{18}$, the compound detected in the tar of coniferous woods by Knauss in 1858 and characterised chemically by Fritzsche and by Fehling in 1860. Little progress had been made up to 1884 in establishing the structure and relationships of the various derivatives of retene. In reviewing the work of previous investigators Hooker suspected, because of

* In the preparation of this sketch the author has been greatly aided by a member of Dr. Hooker's family, Mr. Louis A. Wills of the American Sugar Refining Company, Mr. Sidney J. Osborn of the Great Western Sugar Co., Dr. Louis F. Fieser of Harvard University, and Mr. William W. Shirley of the Pratt Institute Free Library in Brooklyn.

difficulties in combustion, that the reported analytical results were in some cases erroneous. He therefore modified the method of operation by conducting the combustion upon a small sample in the presence of lead chromate: accurate results were secured and progress towards unravelling the structure of retene was thus rapidly advanced. The four articles published by Bamberger and Hooker in 1885 (*Annalen*, **229**, 102; *Ber.*, **18**, 1024, 1030, 1750) described a large number of new derivatives of retene and established the fact that this compound is a phenanthrene derivative with one methyl and one *iso*propyl group, the authors suggesting 8-methyl-5-*iso*propylphenanthrene as a conjectural structure. Subsequent work on retene has been largely in the direction of establishing the exact placement of the two groups indicated by the basic work of Bamberger and Hooker. In 1910 Bucher (*J. Amer. Chem. Soc.*, **32**, 374) proved the structure of retene to be 8-methyl-2-*iso*propylphenanthrene, which corresponds to the 1-methyl-7-*iso*propylphenanthrene of the present scheme of notation. This work upon retene was subsequently of particular value in helping to elucidate the structure of abietic acid.

Hooker's excellent preparation in chemistry and his brilliant research upon retene enabled him to obtain his Ph.D. degree at Munich in the remarkably short period of one year. He had meanwhile come to the conclusion that America offered the best opportunity for his chemical future and immediately after taking his degree came to the United States in the hope of being able to continue his organic research work at one of its universities. Being unsuccessful in this, he obtained a position as chief chemist with the Franklin Sugar Refining Co. in Philadelphia, in the latter part of 1885. This was the beginning of his association with the sugar industry of the United States, a connection which he maintained with great advantage, both to the industry and to himself, during the next 30 years. No evidence of this activity appears, however, in Hooker's publications, as he held that, for competitive reasons, research work done for private industrial enterprises should not be published. He maintained this policy throughout the entire period of his commercial relations and for this reason many improvements in sugar technology which he introduced have been wrongly accredited to others. This restriction of publication did not apply, however, to other subjects and many pieces of research, unrelated to sugar technology and conducted in Hooker's leisure moments, appeared during the years 1887—1896 in the *Berichte*, the *Journal* of the Franklin Institute, the *American Chemical Journal*, and the *Journal* of the London Chemical Society.

Passing over Hooker's minor contributions upon purpurogallin (*Ber.*, 1887, **20**, 3259), reactions of carbazole and pyrrole (*Ber.*, 1888, **21**, 3299), detection of saccharin (*ibid.*, p. 3395), determination of nitrates in potable waters (*ibid.*, p. 3302), and a compound of pyrrole with picric acid (*J. Franklin Inst.*, 1891, **131**, 69), which were presented before the meetings of the Franklin Institute in Philadelphia, we would mention two investigations of major importance which he conducted during this period. The first of these was Hooker's very careful chemical examination of the Philadelphia water supply, the results of which were presented in four reports before the Chemical Section of the Franklin Institute and published in the *Journal* of the Institute for 1889 and 1890 (*J. Franklin Inst.*, **127**, 390, 474; **128**, 66; **129**, 411). The neglect of the Water and Health Departments of Philadelphia in supplying chemical analyses of the municipal water induced Hooker to make this important investigation on his own initiative. His analyses revealed a considerable degree of pollution in the water being pumped from the Delaware River to make up the deficiency in the Schuylkill and Wentz Farm basin supplies for the Kensington district. "What wonder, then," he asks, "that the Kensington district is a very hot-bed of disease in this city?" Hooker's report and recommendations played an important part in rectifying the long-standing evils to which he called the city's attention.

The second chemical research of importance which Hooker conducted during this productive Philadelphia period was his investigation upon lapachol, the first results of which were presented by him and his collaborator, W. H. Greene, before the Chemical Section of the Franklin Institute on April 16th and May 21st, 1889. Hooker's attention had been called to the occurrence of a yellow substance in the pores of Bethabara wood and his examination of its properties proved it to be Paterno's lapacic acid (lapachol). His numerous articles upon the derivatives and constitution of lapachol were published in

the *Journal* of the Franklin Institute (1889, **127**, 387; **128**, 142; 1891, **131**, 56, 61), the *American Chemical Journal* (1889, **11**, 267, 393), the *Berichte* (1889, **22**, 1723), and more exhaustively in the *Journal* of the Chemical Society (1892, **61**, 611; 1893, **63**, 424, 1376; 1894, **65**, 15; 1896, **69**, 1355, 1381). Hooker's investigations caused him to modify the structural formula for lapachol proposed by Paterno, *viz.*, 3-hydroxy-2-Δ^{α}-*iso*pentenyl-1 : 4-naphthaquinone, by shifting the double carbon linkage of the *iso*pentenyl side chain from the Δ^{α}- to the Δ^{β}-position [*i.e.*, to $R{\cdot}CH_2{\cdot}CH{:}C(CH_3)_2$]. The structure assigned to lapachol by Hooker in 1896 was confirmed 30 years later by Fieser's synthesis of this compound (*J. Amer. Chem. Soc.*, 1927, **49**, 857).

Hooker's lapachol investigation led into many ramifications not only upon lapachol itself but upon *iso*lapachol, *iso*-β-lapachol, and lomatiol, and the interesting subject of converting *o*- into *p*- and *p*- into *o*-quinone derivatives (Hooker and Carnell, J., 1894, **65**, 76; Hooker and Walsh, *ibid.*, p. 321). The series of papers upon these subjects show Hooker as a masterful manipulator and endowed with great patience, resourcefulness, and powers of observation.

The lapachol investigation was just opening up a vast field of interesting problems when changes in Hooker's professional connections with the Franklin Sugar Refinery obliged him to suspend for a long time all further research work in organic chemistry. The Franklin Sugar Refining Company was purchased by the American Sugar Refining Company, and it was to this corporation that Hooker's allegiance was transferred in 1892. Hooker, with not a few pangs of regret, packed away his lapachol preparations in order to devote all his thoughts and energies to the work of his new position.

His technological ability is best illustrated by the work which he did for the American beet-sugar industry. When the American Sugar Refining Company acquired a controlling financial interest in many Western beet-sugar factories, Hooker was assigned the important task of organising the technical work of these establishments upon a more efficient basis. The American beet-sugar industry at that time was new and inexperienced. Great difficulties were encountered in operating the Steffen lime saccharate process for recovering sugar from beet-molasses and this was one of the principal problems to which Hooker gave attention. He solved the difficulty by requiring the factories to adopt a finer grinding of the lime. He sought the best mill for this purpose and then by his own improvements perfected it so that it gave the desired results. The elimination of bluing for enhancing the brilliancy of beet-sugars was another reform which Hooker introduced.

In his connection with the beet-sugar industry Hooker manifested rare business ability in contributing to the organisation of the Great Western Sugar Company, of which he was a director from 1909 to 1913. He located several of the important plants of this company and these locations in each instance have proved sound and successful. He showed fine judgment also in the organisation of personnel and of his system of management, which is still largely retained by the company to-day. Hooker is often mentioned as the one who saved the American beet-sugar industry from its previous state of disorganisation and placed it upon a high level of efficiency.

In 1909 Hooker was appointed to the board of directors of the American Sugar Refining Co. and shortly thereafter moved his residence from Philadelphia to Remsen Street, Brooklyn, where he spent his remaining days. It is impossible in this sketch to indicate all that Hooker accomplished in this new position of responsibility. Reference will only be made to his remarkable organising ability, which is shown by the fact that at least seven of the men occupying the highest positions on the technical staff of the American Sugar Refining Company to-day were either originally engaged by him or were selected by him from young men employed by the company. These include three of the superintendents and two of the plant engineers of the Company's five refineries, and two of the five men that comprise the Company's central operating staff in New York.

Hooker had long cherished the plan of retiring from business, as soon as he had acquired a competency, in order to enjoy a well-earned leisure and to realise the fulfilment of certain long-deferred plans. He therefore resigned from the directorship of his company in 1915, thus closing his long productive connection of thirty years with the American sugar industry.

Unlike most men, Hooker was successful in shaping his career almost exactly according to a definite scheme which he had long carried in mind. Having shaken off all business cares and responsibilities, he was ready at the age of 51 to take up with characteristic zest and thoroughness three separate lines of activity in which he had long maintained an interest. The first of these was the resumption of the organic research work upon lapachol which circumstances had caused him to lay aside twenty years before. In the rear of his Brooklyn residence he transformed a former stable into a very complete private laboratory with an electrically operated mill for grinding tropical woods, extraction apparatus, and other equipment necessary for conducting the investigations which he had planned. In visiting Hooker in this laboratory the author was impressed by the quiet satisfaction which he derived from the resumption of his organic research work and also by the pleasure which he manifested in showing to friends his beautiful many-coloured specimens of lapachol derivatives. In contrast, however, with the series of frequent articles that were published in his early period of lapachol research, Hooker adopted in his later period the policy of publishing nothing until the whole investigation was as well finished and accurate as his own high conceptions of completeness and perfection could justify. It is tragic in a way that because of ill health he did not live to see the ultimate realisation of this plan, although he died with the satisfaction of knowing that all the experimental work upon lapachol and lomatiol which he had in mind had been completed and that the work of editing and publishing his results had been left in competent hands. Dr. Louis F. Fieser of Harvard University, whose own researches in this field together with his close associations with Hooker and knowledge of his work render him admirably qualified for the task, has been entrusted with the final preparation of the material for publication. Hooker's final researches upon lapachol will probably be sent to the printer sometime in the present year. In this connection Dr. Fieser writes, " It is remarkable that Dr. Hooker was able to take up his work where he had left off so many years ago and to fulfill the promises implied in his earlier publications; it is still more remarkable that the later work is perhaps even more striking and important than that completed while he enjoyed the full health and vigor of youth."

Another pursuit which engaged much of Hooker's time in this period of business retirement was the building up of his magnificent scientific library. He commenced the accumulation of scientific books early in life and was constantly adding to his collections, even during his period of industrial activity. The enlargement of this library, especially in the acquisition of rare sets of journals, was pursued very energetically by Hooker in his later years, with the result that he finally possessed one of the most complete chemical libraries in the world. It comprises a collection of over 21,000 books, 18,820 of which are volumes of journals.

A third major avocation of Hooker's later years was his interest in magic. It is related that his interest in this subject was first awakened while still a boy in school at Sevenoaks when his father took him to see the performances of Maskelyne and Cooke. He began to give amateur performances in legerdemain at the age of sixteen; but his interest in this field eventually became so strong that he had to put it resolutely aside in order that nothing might interfere with the work in chemistry which he had mapped out for a career. After his retirement, however, Hooker resumed the cultivation of his old hobby with renewed zeal and application. He was no longer content to remain an amateur and with the same thoroughness and attention to detail which he displayed in his chemical and technological work he soon acquired the high degree of proficiency in magic which was his standard in other pursuits. He became a member of the American Society of Magicians and on rare occasions gave private exhibitions before his fellow craftsmen in which feats of levitation and other illusions of his own invention were performed that completely baffled the professional magicians in his audience.

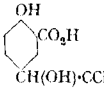
In 1887 Hooker married Mary Elizabeth Owens of Cincinnati, whom he first met in the laboratories of the Royal College of Science at South Kensington where they were fellow students. He is survived by his widow and four children.

C. A. BROWNE.

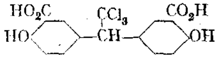
119. *The Condensation of Chloral with Salicylic Acid.*

By Fernando Calvet and Maria N. Mejuto.

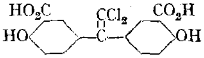
The condensation of chloral with salicylic acid by the action of concentrated sulphuric acid produces 2-*hydroxy*-5-βββ-*trichloro*-α-*hydroxyethylbenzoic acid* (I) and by the reaction of this with a second molecule of salicylic acid, βββ-*trichloro*-4 : 4'-*dihydroxy*-3 : 3'-*dicarboxy*-αα-*diphenylethane* (II).



(I.)



(II.)



(III.)

The acid (I) gives a *monoacetyl* derivative and, by the action of diazomethane, a *methyl* ester, which is easily monoacetylated; the acetyl derivative and the ester of the original acid possess free phenolic hydroxyl groups, as both give colour reactions with ferric chloride. When the acid (I) is heated in concentrated sulphuric acid on the water-bath, hydrogen chloride is evolved and 6-hydroxy*iso*phthalaldehydic acid is obtained, identical with a specimen prepared by the action of chloroform and potash on salicylic acid (Reimer and Tiemann, *Ber.*, 1876, **9**, 1271). The aldehydic acid, which is also produced by the action of methyl-alcoholic potassium hydroxide on the acid (I), is oxidised to the corresponding hydroxy*iso*phthalic acid by potassium permanganate, the constitution of (I) thus being established.

The diphenylethane derivative (II) gives a *dimethyl* ester, which forms a *diacetyl* derivative. When the dimethyl ester is acted upon with boiling methyl-alcoholic potassium hydroxide or cold 30% aqueous potassium hydroxide, the normal hydrolysis of the two methyl groups is accompanied by loss of a molecule of hydrogen chloride, ββ-*dichloro*-4 : 4'-*dihydroxy*-3 : 3'-*dicarboxy*-αα-*diphenylethylene* (III) being produced.

Experimental.

Condensation of Chloral with Salicylic Acid.—A mixture of a freshly prepared solution of 10 g. of salicylic acid in 100 c.c. of concentrated sulphuric acid with 30 g. of chloral hydrate is shaken for ½ hour and poured after 2 days into 800 g. of water containing ice. The viscid colourless mass produced is collected and washed with much cold water; it then becomes microcrystalline, but cannot be recrystallised from any ordinary solvent (yield, 9·8 g.). A solution of the dried product (2 g. in 50 c.c. of methyl alcohol) is twice saturated at 0° with hydrogen chloride, with intermediate boiling, and is finally concentrated to a small bulk; the resinous product crystallises in contact with ethyl alcohol. Recrystallisation from this solvent or, better, acetic acid furnishes βββ-*trichloro*-4 : 4'-*dihydroxy*-3 : 3'-*dicarbomethoxy*-αα-*diphenylethane* (as II) in small nacreous blades, m. p. 200—202° (Found : C, 49·9; H, 3·4; Cl, 24·4. $C_{18}H_{15}O_6Cl_3$ requires C, 49·8; H, 3·5; Cl, 24·6%). The ester is soluble in dilute alkali solution, and develops a cherry-red colour with alcoholic ferric chloride.

The aqueous acid mother-liquor from which the crude diphenylethane derivative (II) has separated is concentrated to half its volume and allowed to cool slowly; 2-*hydroxy*-5-βββ-*trichloro*-α-*hydroxyethylbenzoic acid* (I) then crystallises. Recrystallised from hot water (charcoal), it forms highly refractive, colourless prisms (4·1 g.), m. p. 180—182° (Found : C, 37·7; H, 2·5; Cl, 37·5. $C_9H_7O_4Cl_3$ requires C, 37·8; H, 2·5; Cl, 37·3%). The acid is sparingly soluble in cold water, but dissolves readily in boiling water or in alcohol. The aqueous solution reddens on addition of ferric chloride.

Monoacetyl Derivative and Methyl Ester of 2-*Hydroxy*-5-βββ-*trichloro*-α-*hydroxyethylbenzoic Acid.*—(1) A mixture of the hydroxy-acid (0·7 g.), acetic anhydride (2 c.c.), and sodium acetate is heated on the steam-bath for a short time and kept on a watch-glass; the acetic anhydride slowly absorbs water and a viscid solid separates. This crystallises in contact with cold alcohol and is then recrystallised from aqueous alcohol, the *acetyl* compound forming small colourless leaflets, m. p. 190—192° (Found : C, 40·4; H, 2·6; Cl, 32·6. $C_{11}H_9O_5Cl_3$ requires C, 40·3;

H, 2·8; Cl, 32·5%), which give a cherry-red colour with alcoholic ferric chloride. All attempts to prepare a diacetyl derivative failed.

(2) The finely powdered acid (2·0 g.) is suspended in 12 c.c. of absolute ether and treated with an excess of ethereal diazomethane. During spontaneous evaporation of the ether the *methyl* ester crystallises in tufted needles; recrystallised from dilute alcohol, it forms colourless rhombic tablets (1·2 g.), m. p. 97—99° (Found: C, 39·9; H, 2·8. $C_{10}H_9O_4Cl_3$ requires C, 40·1; H, 3·0%).

The *monoacetyl* derivative of this ester is prepared by means of acetic anhydride and a drop of concentrated sulphuric acid, the mixture being finally heated on the steam-bath and kept on a watch-glass. The resinous substance left after long standing becomes crystalline on treatment with alcohol; it is pressed on a porous plate and twice recrystallised from the same solvent by addition of water to the hot solution. It can also be recrystallised from methyl alcohol, forming colourless prisms, m. p. 90—92° (Found: C, 42·3; H, 2·9. $C_{12}H_{11}O_5Cl_3$ requires C, 42·2; H, 3·2%), which do not give a colour reaction with methyl-alcoholic ferric chloride.

Acetylation of βββ-*Trichloro*-4 : 4′-*dihydroxy*-3 : 3′-*dicarbomethoxy*-αα-*diphenylethane*.—The ester (0·5 g.) is heated with acetic anhydride (2 c.c.) and anhydrous sodium acetate on the steam-bath. The *diacetyl* derivative, precipitated by water and twice crystallised from boiling ethyl alcohol, has m. p. 207—209° (Found: C, 51·3; H, 3·6. $C_{22}H_{19}O_8Cl_3$ requires C, 51·0; H, 3·7%). It is insoluble in water or aqueous alkali, moderately soluble in alcohol, and gives no colour with ferric chloride.

Condensation of 2-*Hydroxy*-5-βββ-*trichloro*-α-*hydroxyethylbenzoic Acid with Salicylic Acid*.—Salicylic acid (1·5 g.) is dissolved in concentrated sulphuric acid (25 c.c.), the substituted benzoic acid (3 g.) added, and the mixture stirred for ½ hour, kept for 1 day, and poured into ice-water. The solid product is boiled in a little alcohol with animal charcoal, and the filtered solution made turbid with water; on cooling, βββ-*trichloro*-4 : 4′-*dihydroxy*-3 : 3′-*dicarboxy*-αα-*diphenylethane* (II) separates in small colourless prisms (1·2 g.), m. p. 290—292° (Found: C, 47·1; H, 2·6. $C_{16}H_{11}O_6Cl_3$ requires C, 47·35; H, 2·7%). Treated with diazomethane or methyl-alcoholic hydrogen chloride, this yields the dimethyl ester already described.

Action of Methyl-alcoholic Potassium Hydroxide on βββ-*Trichloro*-4 : 4′-*dihydroxy*-3 : 3′-*dicarbomethoxy*-αα-*diphenylethane*.—The ester (2 g.) is boiled with 2 g. of potassium hydroxide in 10 c.c. of methyl alcohol for ½ hour, sodium chloride separating. After addition of boiling water (6 c.c.) and removal of the alcohol in steam, the solution is filtered and acidified with hydrochloric acid. The solid product, twice crystallised from dilute alcohol, gives ββ-*dichloro*-4 : 4′-*dihydroxy*-3 : 3′-*dicarboxy*-αα-*diphenylethylene* (III) in prisms, m. p. 295—297° (Found: C, 52·0; H, 2·7. $C_{16}H_{10}O_6Cl_2$ requires C, 52·0; H, 2·7%). This substance does not react with bromine in cold carbon tetrachloride and is not hydrogenated in dilute acetic acid with platinum oxide as catalyst. Treated with diazomethane in ether, it yields the *dimethyl* ester (also produced by the action of methyl-alcoholic hydrogen chloride), which crystallises from alcohol in fine tufted needles, m. p. 120—122° (Found: C, 54·3; H, 3·6. $C_{18}H_{14}O_6Cl_2$ requires C, 54·4; H, 3·5%), soluble in aqueous alkali.

Action of Alcoholic Potassium Hydroxide on 2-*Hydroxy*-5-βββ-*trichloro*-α-*hydroxyethylbenzoic Acid*.—The powdered acid (2 g.) and a solution of 2 g. of potassium hydroxide in 10 c.c. of methyl alcohol are submitted to the treatment described in the preceding paragraph. The 6-hydroxy*iso*phthalaldehydic acid liberated on acidification with hydrochloric acid is extracted with ether, recovered, and recrystallised from hot water, forming plates (0·8 g.), m. p. 248—250° (Found: C, 57·6; H, 3·3. Calc. for $C_8H_6O_4$: C, 57·8; H, 3·6%). The oxime crystallises from hot water in colourless needles, m. p. 179—180° (cf. Fürth, *Ber.*, 1883, **16**, 2182). The aldehydic acid (0·8 g.) in 25 c.c. of acetone is oxidised with potassium permanganate (1·2 g.), the mixture being finally boiled. The precipitate of manganese dioxide and potassium hydroxy*iso*phthalate is extracted with boiling water (3 × 50 c.c.), and this solution acidified with hydrochloric acid; the 4-hydroxy*iso*phthalic acid, recrystallised from water, separates in very fine needles, m. p. 308—310° (decomp.) (Found: C, 52·4; H, 3·35. Calc. for $C_8H_6O_5$: C, 52·7; H, 3·3%). The dimethyl ester has m. p. 96—98° (cf. Jacobsen, *Ber.*, 1878, **11**, 379; Loewenherz, *Ber.*, 1892, **25**, 2796).

Hydroxy*iso*phthalic acid is also obtained when a solution of 1 g. of 2-hydroxy-5-βββ-trichloro-α-hydroxyethylbenzoic acid in 8 c.c. of *N*-sodium hydroxide and 200 c.c. of water is oxidised with 3 g. of potassium permanganate, the mixture being boiled after 24 hours; the filtered liquid is evaporated to 40 c.c. and acidified with hydrochloric acid, and the hydroxy*iso*phthalic acid twice recrystallised from boiling water.

Action of Warm Sulphuric Acid on 2-*Hydroxy*-5-βββ-*trichloro*-α-*hydroxyethylbenzoic Acid*.—A solution of 1 g. of the acid in 10 c.c. of concentrated sulphuric acid is heated on the steam-bath for 10 minutes, hydrogen chloride being evolved, and is then poured into 50 g. of water containing

ice. The solid which separates is recrystallised from methyl alcohol, giving colourless needles of 6-hydroxy*iso*phthalaldehydic acid.

Reduction of 2-Hydroxy-5-βββ-trichloro-α-hydroxyethylbenzoic Acid.—To a mixture of 2 g. of the acid, 16 c.c. of concentrated hydrochloric acid, 15 c.c. of alcohol, and 10 c.c. of water boiling under reflux, 6 g. of granulated zinc are added during 3 hours. The product separates on cooling and is recrystallised from aqueous alcohol, forming needles, m. p. 170—172° (Found : C, 46·3; H, 2·8. $C_9H_6O_3Cl_2$ requires C, 46·35; H, 2·6%). It is vigorously attacked by potassium permanganate in the cold, and has probably the constitution of *2-hydroxy-5-ββ-dichlorovinylbenzoic acid.*

We are indebted to the " Patronato Universitario " of Santiago for a research Fellowship awarded to one of us (M. N. M.), and to Mr. Sánchez-Tella for help in the experimental work.

THE UNIVERSITY, SANTIAGO DE GALICIA. [*Received, November 26th, 1935.*]

120. *The Nitration of 1 : 8-Dihydroxynaphthalene.*

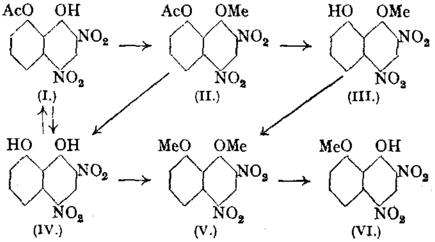
By FERNANDO CALVET and (in part) (MISS) M. C. CARNERO.

ONLY a few disubstituted 1 : 8-dihydroxynaphthalene derivatives of well-established constitution are known, and none suitable for ascertaining the orientation of the nitro-groups in a dinitro-1 : 8-naphthadioxin (Carnero and Calvet, *Anal. Fis. Quim.*, 1934, **32**, 1166). This was our primary reason for studying the nitration of 1 : 8-dihydroxynaphthalene.

1 : 8-Dihydroxynaphthalene is almost completely destroyed in the ordinary methods of nitration. Attempts to prepare 1 : 8-dimethoxynaphthalene gave, in agreement with Staudinger, Schlenker, and Goldstein (*Helv. Chim. Acta*, 1921, **4**, 334; contrast Heller and Kretzschmann, *Ber.*, 1921, **54**, 1106), 1-hydroxy-8-methoxynaphthalene. 1 : 8-Dihydroxynaphthalene was, however, readily diacetylated and also methylenated, and the nitration of these two derivatives is now described.

(1) The action of nitric acid (*d* 1·4) upon 1 : 8-diacetoxynaphthalene at the ordinary temperature produces 2 : 4-*dinitro-1-hydroxy-8-acetoxynaphthalene* (I). Nitration without removal of an acetyl group has not been accomplished. 2 : 4-Dinitro-1-hydroxy-8-acetoxynaphthalene cannot be acetylated or benzoylated, but is easily methylated by diazomethane. 2 : 4-*Dinitro-8-acetoxy-1-methoxynaphthalene* (II), treated with cold dilute aqueous sodium hydroxide, is hydrolysed to 2 : 4-*dinitro-8-hydroxy-1-methoxynaphthalene* (III).

By the action of boiling methyl-alcoholic potassium hydroxide, both 2 : 4-dinitro-1-hydroxy-8-acetoxynaphthalene and 2 : 4-dinitro-8-acetoxy-1-methoxynaphthalene yield 2 : 4-*dinitro-1 : 8-dihydroxynaphthalene* (IV). This can be easily methylated to 2 : 4-*dinitro-1 : 8-dimethoxynaphthalene* (V) by means of diazomethane, but when acetylated it furnishes 2 : 4-dinitro-1-hydroxy-8-acetoxynaphthalene.



2 : 4-Dinitro-1 : 8-dimethoxynaphthalene is easily hydrolysed to 2 : 4-*dinitro-1-hydroxy-8-methoxynaphthalene* (VI) by the action of boiling alcoholic potassium hydroxide. Both

2 : 4-dinitro-1 : 8-dihydroxynaphthalene and 2 : 4-dinitro-1-hydroxy-8-methoxynaphthalene can be reduced to the corresponding diamino-derivatives, only isolable as *dihydrochlorides*.

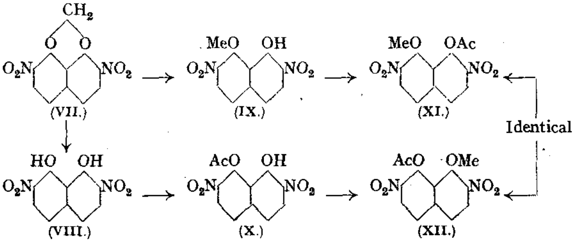
When 2 : 4-diamino-1-hydroxy-8-methoxynaphthalene dihydrochloride is boiled with dilute nitric acid, 3-methoxyphthalic acid is produced, identical with the acid prepared from 3-nitrophthalic acid; its formation establishes the constitutions of 2 : 4-diamino-1-hydroxy-8-methoxynaphthalene, 2 : 4-dinitro-1 : 8-dihydroxynaphthalene, and their derivatives. From 2 : 4-diamino-1 : 8-dihydroxynaphthalene, a *tetrabenzoyl* derivative has been prepared.

(2) The nitration of 1 : 8-methylenedioxynaphthalene by a mixture of equal volumes of fuming nitric acid (*d* 1·5) and glacial acetic acid produces 2(?) : 7(?)-*dinitro*-1 : 8-*methylenedioxynaphthalene* (VII) and 4 : 5-*dinitro*-1 : 8-*methylenedioxynaphthalene*, which are easily separated by fractional crystallisation.

2(?) : 7(?)-Dinitro-1 : 8-methylenedioxynaphthalene is hydrolysed by boiling aqueous *potassium hydroxide and by alcoholic potassium hydroxide to* 2(?) : 7(?)-*dinitro*-1 : 8-*dihydroxynaphthalene* (VIII) and 2(?) : 7(?)-*dinitro*-1-*hydroxy*-8-*methoxynaphthalene* (IX), respectively. These yield the same dinitrodimethoxynaphthalene by the action of diazomethane.

When acetylated with acetic anhydride and sodium acetate, 2(?) : 7(?)-dinitro-1 : 8-dihydroxynaphthalene gives a *monoacetyl* derivative (X) at the ordinary temperature and the diacetyl compound at the boiling point.

If it is assumed that for some structural reason (*e.g.*, an unsymmetrical distribution of the two nitro-groups) there exists a difference in the acidity of the two hydroxyl groups in this dinitrodihydroxynaphthalene, the monomethyl derivative (IX) which results from the action of alcoholic potassium hydroxide on its methylene ether must have its methoxy-group attached in the same position as the acetoxy-group in the acetyl derivative (X), and the product (XI) obtained hy acetylation of the methyl derivative ought to be an isomeride of the substance (XII) prodnced by methylation of the monoacetyl derivative. The two products, (XI) and (XII) are, however, identical. This is the only experimental evidence we can put forward to support the symmetrical constitutions proposed for the dinitro-1 : 8-dihydroxynaphthalene (VIII) and its methylene ether (VII).



2(?) : 7(?)-Dinitro-1 : 8-dihydroxynaphthalene is easily reduced to the diamino-dihydroxynaphthalene, from which a *tetrabenzoyl* derivative has been prepared.

4 : 5-Dinitro-1 : 8-methylenedioxynaphthalene is readily hydrolysed by boiling aqueous potassium hydroxide to 4 : 5-*dinitro*-1 : 8-*dihydroxynaphthalene*, which on reduction gives 4 : 5-diamino-1 : 8-dihydroxynaphthalene, of which the *tetrabenzoyl* derivative was isolated. The constitutions of these substances are established through the identity of this tetrabenzoyl derivative with that obtained by reduction and benzoylation of the bisazo-dye resulting from the coupling of diazotised aniline with 1 : 8-dihydroxynaphthalene (Heller and Kretzschmann, *Ber.*, 1921, **54**, 1102).

EXPERIMENTAL.

Nitration of 1 : 8-*Diacetoxynaphthalene*.—The finely powdered diacetyl derivative (6 g.) (Erdmann, *Annalen*, 1888, **247**, 345, 359; cf. Carnero and Calvet, *loc. cit.*, p. 1157) is slowly added to 30 c.c. of concentrated nitric acid, kept at 25—30°. The crystalline product is washed with water, dried on the steam-bath (yield, 5·4 g.), and recrystallised from boiling acetic acid (charcoal). 2 : 4-*Dinitro*-1-*hydroxy*-8-*acetoxynaphthalene* (I) forms yellow hexagonal prisms, m. p. 200° (*decomp.*) (Found : C, 49·5; H, 2·7; N, 9·6. $C_{12}H_8O_7N_2$ requires C, 49·3; H, 2·7; N, 9·6%), sparingly soluble in alcohol, easily soluble in boiling acetic acid, and soluble in dilute aqueous alkali, from which at higher alkali concentrations the sodium or potassium salt separates in dark red prisms.

2 : 4-*Dinitro*-8-*acetoxy*-1-*methoxynaphthalene* (II).—The 1-hydroxy-compound (I) (2 g.) is added to a slight excess of diazomethane (4 c.c. of nitrosomethylurethane, 11 c.c. of 20% methyl-alcoholic potassium hydroxide, and 350 c.c. of dry ether). The solid remaining after evaporation of the ether is washed with a dilute solution of sodium hydroxide, crystallised from methyl alcohol (charcoal) (yield, 1·25 g.), and recrystallised from methyl or ethyl alcohol, giving pale yellow plates, m. p. 115—117° (Found : C, 51·2; H, 3·0; N, 9·2. $C_{13}H_{10}O_7N_2$ requires C, 51·0; H, 3·25; N, 9·15%), of 2 : 4-*dinitro*-8-*acetoxy*-1-*methoxynaphthalene*, insoluble in water or dilute alkali solution.

2 : 4-*Dinitro*-1 : 8-*dihydroxynaphthalene* (IV).—A solution of 4 g. of potassium hydroxide in 100 c.c. of methyl alcohol is boiled with 2 g. of 2 : 4-dinitro-8-acetoxy-1-hydroxynaphthalene for 1 hour, the alcohol driven off in steam, the dark red potassium salt dissolved in boiling water, and excess of hydrochloric acid added. The 2 : 4-*dinitro*-1 : 8-*dihydroxynaphthalene* obtained crystallises from methyl alcohol or boiling water in brilliant red prisms (1·45 g.), m. p. 180—182° (*decomp.*) (Found : C, 47·9; H, 2·6; N, 11·2. $C_{10}H_6O_6N_2$ requires C, 48·0; H, 2·4; N, 11·2%), sparingly soluble in cold water, rather more soluble in boiling water, giving an orange solution, and slightly soluble in methyl or ethyl alcohol. The dried and finely powdered substance has a distinct sternutatory power. It dyes wool and silk orange. It is very soluble in dilute alkali solutions, but the sparingly soluble *potassium* salt separates on addition of concentrated potassium hydroxide solution; after two crystallisations from boiling water, this forms brilliant scarlet prisms (Found : N, 9·8. $C_{10}H_5O_6N_2K$ requires N, 9·7%). The *silver* salt, prepared from it and the theoretical quantity of silver nitrate in boiling water, crystallises in small violet prisms of metallic sheen (Found : N, 7·7. $C_{10}H_5O_6N_2Ag$ requires N, 7·85%).

2 : 4-*Dinitro*-1 : 8-*dimethoxynaphthalene* (V).—The dihydroxy-compound (3 g.) is treated with ethereal diazomethane and the solid left after spontaneous evaporation of the ether is washed with dilute aqueous sodium hydroxide and twice crystallised from methyl alcohol (charcoal), 2 : 4-*dinitro*-1 : 8-*dimethoxynaphthalene* separating in long, deep yellow prisms or needles (1·7 g.), m. p. 137—139° (Found : C, 51·9; H, 3·7; N, 10·0. $C_{12}H_{10}O_6N_2$ requires C, 51·8; H, 3·6; N, 10·1%), insoluble in water or aqueous alkali, readily soluble in methyl or ethyl alcohol.

2 : 4-*Dinitro*-8-*hydroxy*-1-*methoxynaphthalene* (III).—2 : 4-Dinitro-8-acetoxy-1-methoxynaphthalene (1 g.) is dissolved in a cold solution of 0·5 g. of potassium hydroxide in 50 c.c. of methyl alcohol and after 5—10 minutes an excess of hydrochloric acid is added; 2 : 4-*dinitro*-8-*hydroxy*-1-*methoxynaphthalene* separates in yellow needles, accompanied by a small quantity of scarlet prisms of the monopotassium salt of 2 : 4-dinitro-1 : 8-dihydroxynaphthalene. These are easily removed by recrystallisation from ethyl alcohol, 2 : 4-dinitro-8-hydroxy-1-methoxynaphthalene separating in silky yellow needles (0·5 g.), m. p. 170—171° (Found : C, 49·7; H, 2·7; N, 10·7. $C_{11}H_8O_6N_2$ requires C, 50·0; H, 3·0; N, 10·6%). It dissolves with a cherry-red colour in dilute alkali solution. When boiled with alcoholic potassium hydroxide, it is hydrolysed to 2 : 4-dinitro-1 : 8-dihydroxynaphthalene.

2 : 4-*Dinitro*-1-*hydroxy*-8-*methoxynaphthalene* (VI).—2 : 4-Dinitro-1 : 8-dimethoxynaphthalene (2 g.) is boiled with 180 c.c. of 2*N*-sodium hydroxide for 1½ hours, enough boiling water added to dissolve the separated sodium salt, and the filtered solution strongly acidified with hydrochloric acid; the 2 : 4-*dinitro*-1-*hydroxy*-8-*methoxynaphthalene* obtained (1·6 g.) is recrystallised from boiling alcohol, in which it is only sparingly soluble, and separates in small yellow plates, m. p. 179—180° (decomp.), mixed m. p. with 2 : 4-dinitro-8-hydroxy-1-methoxynaphthalene 145—155° (Found : C, 49·9; H, 3·1; N, 10·7. $C_{11}H_8O_6N_2$ requires C, 50·0; H, 3·0; N, 10·6 %). It dissolves with some difficulty in dilute alkali solutions, producing a red colour. The sodium salt is very sparingly soluble in water.

2 : 4-*Diamino*-1-*hydroxy*-8-*methoxynaphthalene*.—2 : 4-Dinitro-1-hydroxy-8-methoxynaphth-

alene (1·2 g.) is heated with 6 g. of granulated tin and 18 c.c. of concentrated hydrochloric acid on a water-bath for 20 minutes, and a solution of the double salt produced in 15 c.c. of hot water is freed from tin by hydrogen sulphide, cooled in ice, and saturated with hydrogen chloride; 2 : 4-*diamino*-1-*hydroxy*-8-*methoxynaphthalene dihydrochloride* crystallises in thin colourless needles (0·7 g.). It can be purified by solution in a few c.c. of cold water and saturation with hydrogen chloride. In the air, the hydrochloride gradually becomes pink or red; the oxidation is more rapid in solution. For analysis the compound was dried on a porous plate (Found: N, 9·9. $C_{11}H_{12}O_2N_2$,2HCl requires N, 10·1%).

Oxidation of 2 : 4-*Diamino*-1-*hydroxy*-8-*methoxynaphthalene.*—The hydrochloride of the base (1 g.) is boiled under reflux with 3 c.c. of concentrated nitric acid and 9 c.c. of water for 1 hour and an ethereal extract of the product is allowed to evaporate first in the air and then over potassium hydroxide and concentrated sulphuric acid in a vacuum desiccator. The well-formed rhombohedra produced after 2 days are picked out and recrystallised from a few c.c. of boiling water in a vacuum desiccator. 3-Methoxyphthalic acid, obtained in colourless prisms, m. p. 170—171° (gas evolution) (Found: C, 55·3; H, 3·95. Calc. for $C_9H_8O_5$: C, 55·05; H, 4·1%), gives the fluorescein test and is identical (m. p. and mixed m. p.) with the acid prepared from 3-hydroxyphthalic acid (Girardet, *Helv. Chim. Acta*, 1931, **14**, 511), the anhydride of which was methylated with diazomethane (Corbellini and Rossi, *Gazzetta*, 1931, **61**, 281) and the 3-methoxyphthalic anhydride (crystals, m. p. 159—160°, from toluene) hydrolysed with boiling water.

Derivatives of 2 : 4-*Diamino*-1 : 8-*dihydroxynaphthalene.*—The *dihydrochloride*, obtained from the dinitro-compound by the reduction method described above, crystallises in small colourless needles which gradually redden in the air (Found: N, 10·6. $C_{10}H_{10}O_2N_2$,2HCl requires N, 10·65%). The free base is extraordinarily prone to auto-oxidation.

The *tetrabenzoyl* derivative is prepared by shaking a solution of the hydrochloride (0·5 g.), potassium hydroxide (6 g.), and sodium hydrosulphite (2 g.) in water (45 c.c.) with benzoyl chloride (4 g.) for ½ hour. The microcrystalline solid is collected after 12 hours, washed with water, dried on a porous plate and then on a steam-bath, extracted with cold benzene, and crystallised twice from acetic acid (charcoal), small, almost colourless needles (0·5 g.), m. p. 257—258° (decomp.), being obtained (Found: C, 75·4; H, 4·2; N, 4·6. $C_{38}H_{26}O_6N_2$ requires C, 75·25; H, 4·3; N, 4·6%), moderately easily soluble in acetic acid.

Nitration of 1 : 8-*Methylenedioxynaphthalene.*—A solution of 3 g. of the methylene ether (Carnero and Calvet, *loc. cit.*, p. 1164) in 3 c.c. of glacial acetic acid is dropped into a mixture of 9 c.c. of fuming nitric acid (*d* 1·5) and 9 c.c. of glacial acetic acid, appreciable heating being prevented by cooling. After 2 hours, the product which has crystallised is collected and dissolved in 65 c.c. of boiling acetic acid; on cooling, 2(?) : 7(?)-*dinitro*-1 : 8-*methylenedioxynaphthalene* (VII) crystallises in long, pale yellow prisms (1·9 g.), m. p. 198—200° (Found: C, 50·6; H, 2·2; N, 10·6. $C_{11}H_6O_6N_2$ requires C, 50·4; H, 2·3; N, 10·7%), insoluble in water or alkali, but readily soluble in boiling alcohol or acetic acid.

The original acetic acid mother-liquor is concentrated (½ vol.); on slow cooling, a mixture of silky needles and short prisms (of the preceding compound) separates. The needles are picked out and crystallised twice from alcohol, 4 : 5-*dinitro*-1 : 8-*methylenedioxynaphthalene* being obtained in well-formed prisms (0·35 g.), m. p. 177—179° (Found: C, 50·2; H, 2·2; N, 10·8%), insoluble in water or in alkali, moderately easily soluble in alcohol, and easily soluble in acetic acid.

2(?) : 7(?)-*Dinitro*-1 : 8-*dihydroxynaphthalene* (VIII).—The methylene ether (3 g.) is boiled with 200 c.c. of 2*N*-sodium hydroxide for 1 hour, and an excess of concentrated hydrochloric acid added; on cooling, 2(?) : 7(?)-*dinitro*-1 : 8-*dihydroxynaphthalene* separates. Rapidly recrystallised from boiling water, it forms yellowish-green prisms (1·5 g.), m. p. 171—173° (decomp.). The substance usually contains one molecule of water of crystallisation, but was anhydrous when isolated for the first time (Found for anhydrous material: C, 47·9; H, 2·4. $C_{10}H_6O_6N_2$ requires C, 48·0; H, 2·4%. Found for hydrated material: C, 45·1; H, 2·8; N, 10·4. $C_{10}H_6O_6N_2$,H_2O requires C, 44·8; H, 3·0; N, 10·45%). It can be recrystallised from chloroform without losing its water of crystallisation (Found: C, 44·9; H, 2·8; N, 10·25; loss after 5 hours at 110° over phosphoric oxide in a vacuum, 7·6. $C_{10}H_6O_6N_2$,H_2O requires H_2O, 6·7%). It readily forms an orange-red solution in boiling water, but is only sparingly soluble in chloroform; the former solution darkens after some time and the compound is destroyed. The powdered substance is somewhat sternutatory.

The *monoacetyl* derivative is obtained when the dinitrodihydroxynaphthalene (1 g.) reacts with sufficient acetic anhydride to dissolve it; the product is removed after 1 hour and rapidly

recrystallised from warm acetic acid (if boiled or heated with acetic acid for too long, the substance is decomposed), forming yellowish-green polyhedra (0·5 g.), m. p. 125—170° (decomp.). The crystals are dried in a vacuum desiccator (Found : N, 9·2. $C_{12}H_8O_7N_2$ requires N, 9·55%).

The *diacetyl* derivative separates when the dinitrodihydroxynaphthalene is boiled for 5 seconds with a small quantity of acetic anhydride and a trace of sodium acetate; recrystallised from acetic acid, it forms short, well-shaped, pale yellow prisms, m. p. *ca.* 228° (decomp.) (Found : N, 8·5. $C_{14}H_{10}O_8N_2$ requires N, 8·4%), insoluble in water and in aqueous alkali, but sparingly soluble in boiling alcohol.

2(?) : 7(?)-*Dinitro*-1 : 8-*dimethoxynaphthalene* is obtained when the dihydroxy-compound is treated with ethereal diazomethane (see preparation of II and V); twice crystallised from acetic acid, it forms long yellow prisms, m. p. 268—270° (decomp.; after darkening at 250°) (Found : C, 51·8; H, 3·5; N, 10·2. $C_{12}H_{10}O_6N_2$ requires C, 51·8; H, 3·6; N, 10·1%), insoluble in aqueous alkali, sparingly soluble in boiling alcohol, and easily soluble in boiling acetic acid.

2(?) : 7(?)-*Dinitro*-1-*hydroxy*-8-*methoxynaphthalene* (IX).—2(?) : 7(?)-Dinitro-1 : 8-methylenedioxynaphthalene (2 g.) is boiled with 4 g. of potassium hydroxide in 100 c.c. of methyl alcohol for 45 minutes and the red potassium salt is removed, dissolved in boiling water, and acidified with hydrochloric acid, 2(?) : 7(?)-*dinitro*-1-*hydroxy*-8-*methoxynaphthalene* separating in silky yellow needles; recrystallised from acetic acid, it forms greenish-yellow prisms, m. p. 218—220°. Prolonged boiling with acetic acid must be avoided (Found : C, 50·0; H, 3·1; N, 10·6. $C_{11}H_8O_6N_2$ requires C, 50·0; H, 3·0; N, 10·6%). It is practically insoluble in water, soluble in alkali solution, sparingly soluble in boiling methyl or ethyl alcohol, and moderately easily soluble in acetic acid. When methylated with diazomethane in the usual way, it yields 2(?) : 7(?)-dinitro-1 : 8-dimethoxynaphthalene.

2(?) : 7(?)-*Dinitro*-1-*acetoxy*-8-*methoxynaphthalene* (XI and XII) is obtained by the action of warm acetic anhydride and a drop of concentrated sulphuric acid or some anhydrous sodium acetate; recrystallised from warm glacial acetic acid, it forms pale yellow prisms, m. p. 183—185° (Found : C, 50·9; H, 3·2; N, 9·2. $C_{13}H_{10}O_7N_2$ requires C, 51·0; H, 3·3; N, 9·15%). The same compound is formed when 2(?) : 7(?)-dinitro-1-hydroxy-8-acetoxynaphthalene is methylated with diazomethane; m. p. and mixed m. p. 183—185° (Found : C, 50·8; H, 3·2; N, 9·2%).

Reduction of 2(?) : 7(?)-*Dinitro*-1 : 8-*dihydroxynaphthalene*.—The reduction is effected as in the preparation of 2 : 4-diamino-1-hydroxy-8-methoxynaphthalene. The hydrochloride (very small needles) is benzoylated, and the crude product recrystallised from boiling nitrobenzene, the *tetrabenzoyl* derivative separating in long, colourless, hair-like needles, m. p. *ca.* 300° (decomp.). Before analysis, it was well washed with boiling alcohol (Found : N, 4·1. $C_{38}H_{26}O_6N_2$ requires N, 4·6%). It is very sparingly soluble in boiling acetic acid, but dissolves readily in boiling nitrobenzene.

4 : 5-*Dinitro*-1 : 8-*dihydroxynaphthalene*.—4 : 5-Dinitro-1 : 8-methylenedioxynaphthalene (1 g.) is boiled with 70 c.c. of 2*N*-sodium hydroxide for 1 hour and the separated sodium salt is dissolved in boiling water and acidified with hydrochloric acid; recrystallised from methyl alcohol, 4 : 5-*dinitro*-1 : 8-*dihydroxynaphthalene* forms short brown prisms, m. p. (rapidly heated) *ca.* 225° (decomp.) (Found : C, 48·2; H, 2·4; N, 11·2. $C_{10}H_6O_6N_2$ requires C, 48·0; H, 2·4; N, 11·2%), sparingly soluble in water and methyl alcohol but readily in alkali solution.

The *diacetyl* derivative (boiling with acetic anhydride and sodium acetate for a few seconds), after addition of methyl alcohol, crystallises in well-formed brownish-yellow prisms, m. p. 158—160° (Found : N, 8·6. $C_{14}H_{10}O_8N_2$ requires N, 8·4%).

4 : 5-*Dinitro*-1 : 8-*dimethoxynaphthalene*, obtained from the dihydroxy-compound and diazomethane, crystallises from methyl alcohol in fine reddish-brown needles, m. p. 147—150° (decomp., after darkening at 140°) (Found : N, 10·1. $C_{12}H_{10}O_6N_2$ requires N, 10·1%).

Reduction of 4 : 5-*Dinitro*-1 : 8-*dihydroxynaphthalene*.—The *tetrabenzoyl* derivative of 4 : 5-diamino-1 : 8-dihydroxynaphthalene is obtained from 4 : 5-dinitro-1 : 8-dihydroxynaphthalene by the method used in the preparation of the isomeride. Recrystallised from acetic acid, it forms small colourless prisms, m. p. 255—256° (decomp.; after darkening at 245°) (Found : N, 4·35. $C_{38}H_{26}O_6N_2$ requires N, 4·6%).

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121. *Studies in the Synthesis of Vitamin*-A. *Part II.*

By I. M. Heilbron, W. E. Jones, A. Lowe, and H. R. Wright.

In Part I (J., 1935, 584) the preparation of certain intermediates in the proposed synthesis of vitamin-*A* was described, notably α-aldehydo-δ-(2 : 2 : 6-trimethyl-Δ^{6}-*cyclo*hexenyl)-β-methyl-$\Delta^{\alpha\gamma}$-butadiene (I) and β-keto-δ-hydroxy-θ-(2 : 2 : 6-trimethyl-Δ^{6}-*cyclo*hexenyl)-ζ-methyl-$\Delta^{\epsilon\eta}$-octadiene (II). In view of the importance of these as key compounds in the development of the work, a number of additional derivatives have now been prepared. The synthesis itself has also been extended along the lines previously discussed.

(I.) R·CH:CH·CMe:CH·CHO R·CH:CH·CMe:CH·CH(OH)·CH_2·COMe (II.)

$$\left(R = H_2C{<}{}^{CH_2\cdot CMe_2}_{CH_2-CMe}{>}C\cdot\right)$$

The conversion of (II) into β-keto-θ-(2 : 2 : 6-trimethyl-Δ^{6}-*cyclo*hexenyl)-ζ-methyl-$\Delta^{\gamma\epsilon\eta}$-octatriene (III) was difficult to effect owing to the exceptional ease of formation of resinous material under moderately acid conditions. Among the many dehydrating agents tried without success may be mentioned: (a) alcoholic sodium ethoxide (Cherbuliez and Hegar, *Helv. Chim. Acta*, 1932, **15**, 200); (b) distillation from aluminium phosphate (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 533); (c) phosphorus tribromide; (d) distillation from aniline hydrobromide (Kyriakides, *ibid.*, p. 992); (e) heating the acetate with copper-bronze in an inert solvent (Meyer, *Helv. Chim. Acta*, 1935, **18**, 470). Dehydration was ultimately accomplished by means of anhydrous oxalic acid, but even here the reaction could only be carried out satisfactorily with small quantities of the hydroxy-ketone.

Condensation of (III) with ethyl bromoacetate gave *ethyl* θ-(2 : 2 : 6-*trimethyl*-Δ^{6}-cyclo*hexenyl*)-βζ-*dimethyl*-$\Delta^{\alpha\gamma\epsilon\eta}$-*octatetraene*-α-*carboxylate* (IV) as a viscous liquid, which, in contrast to ethyl δ-(2 : 2 : 6-trimethyl-Δ^{6}-*cyclo*hexenyl)-β-methyl-$\Delta^{\alpha\gamma}$-butadiene-α-carboxylate (Karrer, Salomon, Morf, and Walker, *Helv. Chim. Acta*, 1932, **15**, 878), was found to be exceedingly difficult to distil without extensive decomposition, even at a pressure of 0·1 mm. It was accordingly hydrolysed in the cold, but the resultant solid acid could not be obtained pure, since on attempted crystallisation it was partly converted into an alkali-insoluble material. This behaviour is paralleled by the tendency towards decarboxylation exhibited by δ-phenyl-β-methyl-$\Delta^{\alpha\gamma}$-butadiene-α-carboxylic acid (Kohler and Heritage, *Amer. Chem. J.*, 1910, **43**, 485) and the difficulty experienced in purifying $\Delta^{\alpha\gamma\epsilon\eta}$-decatetraenoic acid (Reichstein, Amman, and Trivelli, *Helv. Chim. Acta*, 1932, **15**, 263). For analysis a portion of the crude acid was converted into its *methyl* ester, which was purified by slow distillation at 2×10^{-4} mm., from a retort heated in an electrically controlled furnace.

Conversion of the barium salt of the acid from (IV) into the corresponding aldehyde by the method employed in the preparation of (I) is now under investigation.

(III.) R·CH:CH·CMe:CH·CH:CH·COMe
(IV.) R·CH:CH·CMe:CH·CH:CH·CMe:CH·CO_2Et
(V.) R·CH:CH·CMe:CH·CH(OH)·CH_2·CMe:CH·CO_2Et
(VI.) R·CH:CH·CMe(OH)·C:CH

The hydroxy-ketone (II) has been condensed with ethyl bromoacetate to *ethyl* δ-*hydroxy*-θ-(2 : 2 : 6-*trimethyl*-Δ^{6}-cyclo*hexenyl*)-βζ-*dimethyl*-$\Delta^{\alpha\epsilon\eta}$-*octatriene*-α-*carboxylate* (V), which was hydrolysed and converted into the barium salt in the usual manner. Distillation of the latter with barium formate at 2×10^{-4} mm. gave α-*aldehydo*-δ-*hydroxy*-θ-(2 : 2 : 6-*trimethyl*-Δ^{6}-cyclo*hexenyl*)-βζ-*dimethyl*-$\Delta^{\alpha\epsilon\eta}$-*octatriene* (*phenylsemicarbazone*, m. p. 181—182°) and not, as had been hoped, α-aldehydo-θ-(2 : 2 : 6-trimethyl-Δ^{6}-*cyclo*hexenyl)-βζ-dimethyl-$\Delta^{\alpha\gamma\epsilon\eta}$-octatetraene.

A further unsuccessful attempt has been made to convert ε-(2 : 2 : 6-trimethyl-Δ^{6}-*cyclo*hexenyl)-γ-methylpent-δ-en-α-yn-γ-ol (VI) (see Part I) into the aldehyde (I). Descriptions are given in French Patents 671,558 and 770,154 (*Chem. Zentr.*, 1930, II, 134; 1935, I,

632) for the preparation of vinyl acetate and ethylidene diacetate by the condensation of acetylene with acetic acid in the presence of the mercury salt of naphthalene-2 : 7-disulphonic acid. Treated in the same manner, (VI) gave a semi-solid product, probably a mixture of the mono- and the di-acetate, which distilled steadily over a wide range. The whole was accordingly hydrolysed directly with cold alkali, which theoretically could give rise to either (VII) or (VIII) depending on the mode of addition of the acetic acid at the acetylene linkage; whereas the former might be expected readily to dehydrate on heating, such is not possible with (VIII). The compound actually obtained was not the aldehyde (I) and the analysis of its *phenylsemicarbazone*, m. p. 176—178°, agrees with that required for the derivative of the hydroxy-ketone (VIII), although this does not completely eliminate the possibility of (VII).

(VII.) R·CH:CH·CMe(OH)·CH_2·CHO R·CH:CH·CMe(OH)·COMe (VIII.)

Experimental.

*α-Aldehydo-δ-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-β-methyl-$\Delta^{\alpha\gamma}$-butadiene* (I).—The following additional derivatives have been prepared: (a) the p-*tolylsemicarbazone* (method of Sah and Lei, *J. Chinese Chem. Soc.*, 1934, **2**, 168), fine needles from alcohol, m. p. 172—173° (Found: C, 75·9; H, 8·4; N, 11·8. $C_{23}H_{31}ON_3$ requires C, 75·6; H, 8·55; N, 11·6%); (b) the p-*chlorobenzoylhydrazone* (cf. Shih and Sah, *Sci. Reports Nat. Tsing Hua Univ.*, 1934, **2**, 354), plates from alcohol, m. p. 202—203° (Found: C, 71·0; H, 7·4; N, 7·7; Cl, 9·7. $C_{22}H_{27}ON_2Cl$ requires C, 71·2; H, 7·2; N, 7·6; Cl, 9·6%).

*β-Keto-δ-hydroxy-θ-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-ζ-methyl-$\Delta^{\epsilon\eta}$-octadiene* (II).—This compound, prepared as described in Part I, yields a p-*tolylsemicarbazone* crystallising from alcohol in short needles, m. p. 168—169° (Found: C, 74·0; H, 8·6; N, 10·2. $C_{26}H_{37}O_2N_3$ requires C, 73·8; H, 8·8; N, 10·0%), and a p-*chlorobenzoylhydrazone*, which separates from alcohol in pearly plates with a greenish reflex, m. p. 204° (Found: C, 69·8; H, 7·5; N, 6·8; Cl, 8·6. $C_{25}H_{33}O_2N_2Cl$ requires C, 70·0; H, 7·75; N, 6·5; Cl, 8·3%).

The *o*-chlorobenzoylhydrazones of both (I) and (II) were unsuitable for characterisation owing to their excessive solubilities.

*β-Keto-θ-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-ζ-methyl-$\Delta^{\gamma\epsilon\eta}$-octatriene* (III).—β-Keto-δ-hydroxy-θ-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-ζ-methyl-$\Delta^{\epsilon\eta}$-octadiene (II) (2 g.) was heated at 160° (oil-bath temperature) with freshly dehydrated oxalic acid (5 g.) for 1½ hours and the whole was then steam-distilled in nitrogen, whereby unchanged hydroxy-ketone was removed. The residnal solid was extracted with ether, the extract dried over sodium sulphate, and the major portion of the solvent removed. Alcohol was then added, and the *ketone* precipitated by cooling in solid carbon dioxide–acetone. After repeated crystallisation from alcohol at − 50° it was obtained as a pale yellow solid softening at 138° and melting completely at 144°; it gave a violet-red colour with chloroformic antimony trichloride (Found: C, 83·8; H, 10·4. $C_{18}H_{26}O$ requires C, 83·7; H, 10·1%).

*Ethyl θ-(2 : 2 : 6-Trimethyl-Δ^6-*cyclo*hexenyl)-βζ-dimethyl-$\Delta^{\alpha\gamma\epsilon\eta}$-octatetraene-α-carboxylate* (IV).—A solution of the above ketone (5 g.) and ethyl bromoacetate (3·3 g.) in benzene (40 c.c.) was added rapidly to zinc needles (1·3 g.) covered with boiling benzene (20 c.c.), and the reaction completed by refluxing for 3 hours in an atmosphere of nitrogen. After being filtered rapidly in a stream of nitrogen (the product at this state is extremely sensitive towards oxidation), the solution was decomposed by shaking with 10% acetic acid (50 c.c.), and the whole extracted with light petroleum (b. p. 40—60°). The washed extract was dried over sodium sulphate and after removal of solvent the dark semi-solid residue was heated for 20 minutes at 180°/20 mm. to effect dehydration of the β-hydroxy-ester. Distillation of a portion of the product at 2 × 10^{-4} mm. gave two fractions: (a) a small quantity of a yellow oil, b. p. *ca.* 150°, consisting of almost pure *ester* (IV) (Found: C, 81·3; H, 10·1. $C_{22}H_{32}O_2$ requires C, 80·5; H, 9·9%); and (b) an orange-red oil, b. p. *ca.* 180°, which set to a hard resin on standing (Found: C, 85·5; H, 10·4%). The main portion of the crude undistilled ester (5 g.), dissolved in the minimum quantity of ether, was added to 10% alcoholic potassium hydroxide (20 c.c.), and the mixture rendered homogeneous by gradual addition of ether. After standing for 24 hours at room temperature, the red solution was diluted with water and thoroughly extracted with ether. The aqueous layer was rendered slightly acid with dilute phosphoric acid and extracted with ether, and the extract washed and dried over sodium sulphate. The solid acid obtained on evaporation of the solvent could not be obtained sufficiently pure for analysis.

Methyl θ-(2 : 2 : 6-*Trimethyl*-Δ^6-cyclo*hexenyl*)-βζ-*dimethyl*-$\Delta^{\alpha\gamma\epsilon\eta}$-*octatetraene*-α-*carboxylate.*—A solution of the above acid (1 g.) in aqueous potassium hydroxide (0·2 g. in 100 c.c. of water) was treated with methyl sulphate (0·3 g.), and the whole shaken for 2 hours in an atmosphere of nitrogen. Further quantities of potassium hydroxide solution (0·2 g. in 5 c.c. of water) and methyl sulphate (0·3 g.) were added after 2 and 4 hours and shaking was continued for a further 12 hours. The suspension was then thoroughly extracted with light petroleum (b. p. 60—80°) and filtered from a small quantity of semi-solid material, and the filtrate dried over sodium sulphate. The oil obtained after removal of the solvent was distilled at 2 × 10^{-4} mm., giving the *methyl* ester as a pale yellow, viscous oil, b. p. 135—140° (Found : C, 80·1; H, 9·7. $C_{21}H_{30}O_2$ requires C, 80·2; H, 9·6%).

Ethyl δ-*Hydroxy*-θ-(2 : 2 : 6-*trimethyl*-Δ^6-cyclo*hexenyl*)-βζ-*dimethyl*-$\Delta^{\alpha\epsilon\eta}$-*octatriene*-α-*carboxylate* (V).—β-Keto-δ-hydroxy-θ-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-ζ-methyl-$\Delta^{\epsilon\eta}$-octadiene (II) (10 g.) was condensed with ethyl bromoacetate (6 g.) as described in Part I for the similar reaction with β-ionone. The product was a yellow oil, b. p. 90—150°/4 mm., which on redistillation was separated into two fractions : (a) 2·5 g., b. p. 95—130°/4 mm., consisting mainly of unchanged hydroxy-ketone; (b) 8·0 g., b. p. 135—145°/4 mm. Redistillation of the latter gave the pure *hydroxy-ester* (V) as a pale yellow oil, b. p. 140—142°/4 mm. (Found : C, 76·0; H, 10·0. $C_{22}H_{34}O_3$ requires C, 76·3; H, 9·9%).

α-*Aldehydo*-δ-*hydroxy*-θ-(2 : 2 : 6-*trimethyl*-Δ^6-cyclo*hexenyl*)-βζ-*dimethyl*-$\Delta^{\alpha\epsilon\eta}$-*octatriene.*—The above ester was converted into the barium salt of the corresponding acid as described in Part I for ethyl δ-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-β-methyl-$\Delta^{\alpha\gamma}$-butadiene-α-carboxylate. A finely sieved mixture of the dry barium salt (2·5 g.) and barium formate (2·3 g.) was evenly diluted with an equal bulk of silver sand, and the whole distilled in the apparatus mentioned in the theoretical section (temperature 180°, pressure 2 × 10^{-4} mm.). The aldehyde, an orange-yellow, fairly mobile oil, was converted into its *phenylsemicarbazone*, which crystallised from alcohol in needles, m. p. 181—182° (Found : C, 74·2; H, 8·5; N, 10·0. $C_{27}H_{37}O_2N_3$ requires C, 74·4; H, 8·5; N, 9·7%).

Action of Acetic Acid on ε-(2 : 2 : 6-*Trimethyl*-Δ^6-cyclo*hexenyl*)-γ-*methylpent*-δ-*en*-α-*yn*-γ-*ol* (VI).—A solution of (VI) (8 g.), prepared as previously described (see Part I), in glacial acetic acid (50 c.c.) was added during ½ hour to a well-stirred suspension of mercuric oxide (0·5 g.) and naphthalene-2 : 7-disulphonic acid (5 g.) in glacial acetic acid (50 c.c.) at 30—40°. After 2 hours the temperature was raised to 70—80° for a further 2 hours; the reaction mixture was then cooled, poured into water, and neutralised with sodium carbonate. The resultant brown oil, which was extracted with ether and worked up in the usual manner, distilled steadily over a range (120—140°/5 mm.). The total distillate was hydrolysed by treatment at room temperature with 5% alcoholic potassium hydroxide (100 c.c.); after dilution with water, the whole was ether-extracted, and the extract dried over sodium sulphate. Removal of the solvent gave an oil, which was first heated at 150°/20 mm. for ½ hour and then distilled, yielding a yellowish-orange mobile oil, b. p. 90—100°/2 mm., giving a *phenylsemicarbazone*, which crystallised from alcohol in needles, m. p. 176—178° (Found : C, 71·9; H, 8·4; N, 11·4. $C_{22}H_{31}O_2N_3$ requires C, 71·6; H, 8·4; N, 11·4%).

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122. *Methylalkoxyglyoximes as Chelate Groups.*

By E. Sharratt and W. Wardlaw.

In a recent investigation (this vol., p. 129) we isolated as green crystalline substances four complexes of the type (I). These were obtained from the reaction [*e.g.*, (A)] between anhydrous cupric chloride and a glyoxime in ethyl-alcoholic solution. When dimethyl-, methylethyl-, or benzylmethyl-glyoxime was used, only one product resulted in each case, but with monomethylglyoxime the reaction was more complex. From the mixture of the cold concentrated alcoholic solutions of (anhydrous) cupric chloride and methylglyoxime, (I) crystallised within an hour as already described. It has since been found that the

mother-liquor afforded emerald-green crystals (II) during the course of the next few days; these differed from (I), not only in colour, but also in that they were soluble in benzene and in chloroform, and a preliminary analysis suggested that (II) was (I) with alcohol of crystallisation. However, it was not possible to remove alcohol from (II), either by maintaining it at 100° for some hours or by placing it in a vacuum desiccator over calcium chloride for a week. Moreover, a complete analysis of (II) revealed that the molecule had only 10 hydrogen atoms instead of the 12 demanded by the structure suggested above. Further investigation indicated that the *product* (II) had an entirely different constitution from that of (I). A new chelate group (III) had been formed in the reaction, and had produced the co-ordination compound (II). The experimental data upon which these formulæ are based are as follows.

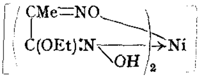
When an alcoholic solution of (II) was treated with aqueous sodium sulphide [reaction (C)], and the copper sulphide removed, the new *oxime* (III) was isolated from the filtrate as a white substance which crystallised from chloroform in silky needles. It was soluble in benzene, acetone, and alcohols, but only slightly soluble in water. With nickel salts it gave an orange-yellow *compound* (V), which melted without decomposition at 197°—a reaction typifying its glyoxime structure. If (I) was similarly treated with sodium sulphide, the original methylglyoxime was liberated, and isolated as its characteristic nickel derivative (see table; also Tschugaeff, *Chem. Zentr.*, 1911, **82**, i, 871).

$$\left[\begin{matrix}\text{CMe:N·OH}\\ \text{CH=N·OH}\end{matrix}\right] + CuCl_2 = \left[\begin{matrix}\text{CMe:N·OH}\\ |\\ \text{CH=N·OH}\end{matrix} \rightarrow Cu \begin{matrix}Cl\\ Cl\end{matrix}\right] \quad (I.) \quad (A)$$

$$(I) + EtOH + \tfrac{1}{2}O_2 = H_2O + \left[\begin{matrix}\text{CMe=N·OH}\\ |\\ \text{C(OEt):N·OH}\end{matrix} \rightarrow Cu \begin{matrix}Cl\\ Cl\end{matrix}\right] \quad (II.) \quad (B)$$

$$(II) + Na_2S = CuS + 2NaCl + \left[\begin{matrix}\text{CMe=N·OH}\\ \text{C(OEt):N·OH}\end{matrix}\right] \quad (III.) \quad (C)$$

$$(III) + H_2O + HCl = NH_2OH,HCl + \left[\begin{matrix}\text{CMe=N·OH}\\ \text{C(OEt):O}\end{matrix}\right] \quad (IV.) \quad (D)$$



(V.)

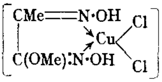
When (II) was decomposed with hydrogen sulphide, the filtrate obtained on removal of copper sulphide and excess of gaseous reagent produced no precipitate with nickel acetate, but gave, on concentration, hydroxylamine hydrochloride and ethyl α-oximinopropionate (IV), identified by comparison with the ester synthesised from pyruvic acid (Meyer and Janny, *Ber.*, 1882, **15**, 1527). Product (I), when decomposed with aqueous hydrogen sulphide, again yielded the original methylglyoxime. These experimental results indicate the above scheme of reactions.

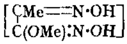
If decomposition (C) is effected with hydrogen sulphide, instead of the sodium salt, free hydrochloric acid is liberated, which hydrolyses (III), as shown in (D). According to this scheme, (II) should be formed only in the presence of an oxidising agent such as air. We find that, by exclusion of air, product (I) alone results from the reaction between cupric chloride and methylglyoxime in ethyl alcohol. Moreover, (I) should be convertible into (II) on treatment with alcohol, and this proves to be the case if free access of air is permitted [reaction (B)].

When other compounds of type (I), *i.e.*, from dimethyl-, methylethyl-, or benzylmethylglyoxime, were used, there was no evidence of any reaction, even after refluxing with ethyl or methyl alcohol for seven hours. The absence of such reaction is readily understood from the mechanism suggested for the production of (II). This substance is obtained from (I) by a process involving the elimination of the elements of water, one hydrogen atom being

obtained from the glyoxime molecule itself. As no other compound of type (I) contains a hydrogen atom in the requisite position, such a reaction could not occur with these compounds—in fact, the non-formation of such substances affords an interesting proof that the explanation offered is correct.

In order to determine whether the reactions for the formation of (II) were general, methyl alcohol was substituted for ethyl alcohol. On mixing cupric chloride and methylglyoxime in this solvent, no material separated until, after three days, the *product* (VI) commenced to crystallise. Analysis of this substance indicated that it was the analogue of (II). The non-precipitation of (I) is due to its greater solubility in methyl than in ethyl alcohol.

(VI.) 

 (VII.)

Decomposition of (VI) with sodium sulphide produced *methylmethoxyglyoxime* (VII), whereas hydrogen sulphide gave hydroxylamine hydrochloride and methyl α-oximinopropionate.

Compounds (III) and (VII) may readily be distinguished from the dialkylglyoximes, especially by means of their *nickel* derivatives :

Glyoxime	Monomethyl.	Dimethyl.*	Methylethyl.	Methylmethoxy.	Methylethoxy.
M. p.	154°	236° (decom.)	170°	148°	142°
		Nickel derivatives.			
	Deep crimson, readily reverting to orange (decomp. 243°).	Crimson; sublimes at 250°.	Tangerine (decomp. 260°).	Orange; reverts to yellow at 223° (decomp. 285°).	Orange-yellow (m.p. 197°).

* Tschugaeff, *Z. anorg. Chem.*, 1905, **46**, 145.

The two new organic compounds (III) and (VII) are oxime derivatives of esters (*viz.*, ethyl and methyl α-oximinopropionates). Alternatively, they may be regarded as esters of substituted hydroxamic acids, and it is most interesting that their preparation involves an oxidation, as does that of the hydroxamic acids themselves from nitroxyl and aldehydes (Angeli and Angelico, *Gazzetta*, 1904, **34**, i, 50) :

$$R{\cdot}CHO + HN(OH)_2 = R{\cdot}C(OH){:}N{\cdot}OH + H_2O.$$

Experimental.

Copper Methylethoxyglyoxime Dichloride (II).—Copper methylglyoxime dichloride (I) was prepared as already described (this vol., p. 131), and the filtrate was set aside in a vessel so as to permit access of air. Emerald-green needles began to separate after 24—30 hours; 6 hours later they were removed, further yields being removed daily. The needles were washed with a little alcohol, and dried; m. p. 165° (decomp.) [Found : Cu, 22·68; Cl, 25·22; N, 9·8; C, 21·22; H, 3·6. $C_5H_{10}O_3N_2,CuCl_2$ requires Cu, 22·67; Cl, 25·28; N, 9·98; C, 21·39; H, 3·59%. $C_5H_{12}O_3N_2,CuCl_2$, *i.e.*, (I) with EtOH of crystallisation, would require Cu, 22·51; Cl, 25·10; N, 9·91; C, 21·24; H, 4·28%]. On recrystallisation from acetone, chloroform, or benzene, (II) separated unchanged in emerald-green needles (Found : from acetone, Cu, 22·5; from benzene, Cl, 24·9%). A sample of (II) was placed on a small dry watch-glass, and the total weight recorded (4·7632 g.); after 6 hours' heating at 100°, no change in weight could be detected (4·7631 g.). Analysis of a fraction of the *dichloride* (II) which had been kept over calcium chloride in a vacuum desiccator for a week again proved that it was unaltered (Found : Cl, 25·12%).

Like other similar complexes of type (I), substance (II) was decomposed by water, and the results of molecular-weight determinations in phenol and electrical-conductivity measurements in acetone prove it to be a true 4-covalent compound.

Cryoscopic determination in phenol (constant = 7·27° per 1000 g.) : 6·29 g. per 1000 g. gave Δt = 0·190°, whence M = 241 (Calc. : 281).

Conductivity. A solution in acetone (3·620 g./l.) had κ = 3·471 × 10^{-5} mho at 25°, whence μ = 2·69.

Attempted Preparation of (II) *in Absence of Air.*—A solution of copper chloride and methylglyoxime in ethyl alcohol, in the same proportions as in the foregoing experiment, was placed in a flask with exclusion of air. Product (I) separated rapidly as before, but was allowed to remain, since its removal would necessitate exposure of the mother-liquor to air. A week later, there was no sign of any further reaction, and the product then removed consisted solely of (I) (Found: Cu, 27·0; Cl, 29·9%). The filtrate was then divided into two fractions, and to one free access of air was permitted; from this, emerald-green needles characteristic of (II) appeared after 30—36 hours, but from the fraction from which air was excluded no crystals separated.

Copper Methylmethoxyglyoxime Dichloride (VI).—A cold solution of anhydrous copper chloride (1 g.) in methyl alcohol (40 c.c.) was mixed with a solution of methylglyoxime (1 g.) in the same solvent. After 3 days, bright emerald-green crystals appeared. These were removed four days later, and dried; m. p. 176° (decomp.) (Found: Cu, 23·6; Cl, 26·67; C, 18·0; H, 3·2. $C_4H_8O_3N_2,CuCl_2$ requires Cu, 23·8; Cl, 26·61; C, 18·0; H, 3·0%). The *substance* was only slightly soluble in chloroform and in benzene, and not readily soluble in acetone [contrast (II)].

Methylethoxyglyoxime (III).—A solution of the crystals (II) in ethyl alcohol (0·2 g. in 20 c.c.) was treated with aqueous sodium sulphide (0·2 g.; 5 c.c.). After removal of the precipitated copper sulphide, the filtrate was evaporated to dryness, and the residual *glyoxime* twice recrystallised from chloroform or benzene; m. p. 142° (Found: C, 40·8; H, 7·0; N, 19·4. $C_5H_{10}O_3N_2$ requires C, 41·1; H, 6·0; N, 19·2%). Reaction of the oxime with nickel acetate in aqueous-alcoholic solution gave an orange-yellow precipitate of the *nickel* derivative [Found: Ni, 16·8. $(C_5H_9O_3N_2)_2Ni$ requires Ni, 16·8%]. After recrystallisation from alcohol, this melted to a red liquid at 197° without decomposition.

Methylmethoxyglyoxime (VII).—Decomposition of (VI) with sodium sulphide in a similar manner to that just described yielded *methylmethoxyglyoxime* as a white solid, crystallising from chloroform in silky needles, m. p. 148° (Found: C, 36·23; H, 5·8; N, 20·9. $C_4H_8O_3N_2$ requires C, 36·36; H, 6·11; N, 21·2%). On addition of an alcoholic solution of this oxime to aqueous nickel acetate, an orange precipitate of the *nickel* complex was obtained; it was recrystallised from alcohol [Found: Ni, 18·5. $(C_4H_7O_3N_2)_2Ni$ requires Ni, 18·3%].

Decomposition of (I), (II), *and* (VI) *with Hydrogen Sulphide.*—The sap-green crystals (I) (0·2 g.) were dissolved in cold alcohol (20 c.c.), and the solution diluted with an equal volume of water. Hydrogen sulphide was then passed through the solution till precipitation of the metal was complete. The mixture was boiled and filtered, excess hydrogen sulphide and copper sulphide thus being removed. Addition of aqueous nickel and ammonium acetates to the cold filtrate produced a scarlet precipitate which became orange after an hour, or on heating. This reaction proves the presence of the original methylglyoxime in the filtrate, and so establishes formula (I).

Similar treatment of substances (II) and (VI) with hydrogen sulphide produced filtrates which did not react with nickel acetate. These solutions were therefore evaporated to dryness, and the resulting residues extracted with a little alcohol. The undissolved material in both cases proved to be hydroxylamine hydrochloride. The alcoholic extracts were evaporated, and the white solid so obtained twice recrystallised from light petroleum (b. p. 60—80°). The colourless needles so produced proved to be respectively ethyl (m. p. 95°) and methyl (m. p. 71°) α-oximinopropionates (Found, for ethyl ester: C, 45·97; H, 7·08; N, 11·3. Calc. for $C_5H_9NO_3$: C, 45·80; H, 6·92; N, 10·7%. Found, for methyl ester: N, 12·4. Calc. for $C_4H_7NO_3$: N, 12·0%); for the latter, Lepercq (*Bull. Soc. chim.*, 1894, 11, 299) gives m. p. 69°.

Ethyl α-Oximinopropionate (IV).—This ester was synthesised by a modification of Meyer and Janny's method (*loc. cit.*). Aqueous solutions of hydroxylamine hydrochloride (10 g.; 30 c.c.) and lead nitrate (24 g.; 50 c.c.) were mixed, and the resulting lead chloride removed. Sodium hydroxide solution (30 c.c.; 5*N*) was added to the filtrate, and lead hydroxide was filtered off. The filtrate was mixed with pyruvic acid (10 g.) dissolved in sodium hydroxide (80 c.c.; 5*N*), and the cooled solution set aside over-night and then twice extracted with ether (50 c.c.) to remove impurities. The aqueous solution was acidified with acetic acid (20 c.c.; 5*N*), and silver nitrate solution (25 g.; 60 c.c.) added. The voluminous white precipitate of silver α-oximinopropionate which resulted was removed by filtration, care being taken to minimise access of light to the substance. After being washed with water, the silver salt was transferred to a desiccator (containing calcium chloride), which was then evacuated and placed in a dark cupboard for a week. The dried silver salt (10 g.) was then mixed with ethyl iodide (20 g.) and alcohol (30 c.c.), the whole being heated under reflux for 3 hours. After silver iodide had been separated, the solvent was removed by distillation, and the residue recrystallised twice from light petroleum (Found: C, 46·1; H, 6·8%).

A sample of the ester thus synthesised was melted with a similar amount of the ester (IV) obtained by decomposition of (II), and the mixed melt cooled. Samples of this mixture and of the two separate substances were heated together in an oil-bath: all three melted simultaneously at 95° (Meyer and Züblin, *Ber.*, 1878, **11**, 693, give 94°; Meyer and Janny give 95°).

Treatment of Compounds of Type (I) *with Alcohols.*—Copper methylglyoxime dichloride (I) (1 g.) was heated under reflux with ethyl alcohol (50 c.c.) for an hour. The hot solution was then filtered, and emerald-green needles separated later; these were identical with (II) (Found: Cl, 25·1%).

The other three compounds of type (I) were similarly treated with ethyl alcohol, but even after 7 hours no reaction could be observed. Methyl alcohol was also used as solvent, but in no case was there any indication of reaction: copper dimethylglyoxime dichloride was recovered unchanged (Found: Cu, 25·6. Calc.: Cu, 25·4%) and so also was the methylethyl analogue (Found: Cu, 23·7. Calc.: Cu, 24·0%).

We thank Dr. E. Oliver for numerous micro-analyses (C, H, and N) and Dr. E. L. Hirst, F.R.S., and Dr. C. R. Porter for helpful discussion. We are also indebted to the Department of Scientific and Industrial Research for a grant to one of us (E. S.).

THE UNIVERSITY, EDGBASTON, BIRMINGHAM. [*Received, February 20th*, 1936.]

123. *Methoxylated* o-*Benzoylbenzoic Acids.*

By CH. WEIZMANN and ERNST BERGMANN.

FOR the synthesis of substituted *o*-benzoylbenzoic acids from phthalic anhydrides, two methods are available, *viz.*, the Friedel–Crafts reaction and the reaction with Grignard compounds (Weizmann and co-workers, J., 1935, 1367). Our interest in the synthesis of methoxylated *o*-benzoylbenzoic acids was their relation to hydroxylated anthraquinones and the extent, if any, to which demethylation occurs in the Friedel–Crafts reaction.

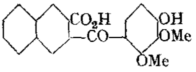
(1) According to the literature α-naphthyl methyl ether condenses with phthalic anhydride in presence of aluminium chloride to give *o*-(4′-hydroxy-1′-naphthoyl)benzoic acid (Fieser and Dietz, *J. Amer. Chem. Soc.*, 1929, **51**, 3141), and β-naphthyl methyl ether yields *o*-(2′-methoxy-1′-naphthoyl)benzoic acid (Knapp, *Monatsh.*, 1934, **60**, 189; Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 3546) or the demethylated compound (compare also Cohn, *Pharm. Zentr.*, 1914, **55**, 744). We obtained, at room temperature, the methoxylated acids in both cases. The structure of the keto-acid obtained from β-naphthyl methyl ether was proved by its synthesis from phthalic anhydride and the magnesium derivative of 1-bromo-2-naphthyl methyl ether. Condensation between 1 : 5-dimethoxynaphthalene and phthalic anhydride gave *o*-(1′ : 5′-dimethoxy-4′-naphthoyl)benzoic acid, reaction being assumed to take place in the 4′-position (compare the reaction with diazotised aniline and similar substances; Fischer and Bauer, *J. pr. Chem.*, 1916, **94**, 22; 1916, **95**, 261): the product readily gave the 8′-acetyl compound on treatment with acetic anhydride.

If the interaction between the components is smooth, aluminium chloride obviously combines with the formed carbonyl group before it can exert its demethylating action. Where reaction is rather slow, demethylation occurs; *e.g.*, pyrogallol trimethyl ether reacts with naphthalene-2 : 3-dicarboxylic anhydride and with hemipinic anhydride to produce (I) and (II), respectively, the positions of the acyl groups again being assumed. Undemethylated products are obtainable by means of 4-lithio-1 : 2 : 3-trimethoxybenzene (method of Ziegler and Colonius, *Annalen*, 1930, **479**, 135), which, *e.g.*, gives *o*-(2′ : 3′ : 4′-trimethoxybenzoyl)benzoic acid on reaction with phthalic anhydride. 4-Iodo-1 : 2 : 3-trimethoxybenzene does not react with magnesium.

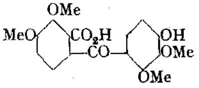
(2) From hemipinic anhydride and phenylmagnesium bromide, an acid was obtained which was apparently identical with the dimethoxybenzoylbenzoic acid produced by oxidation of phenyldihydroberberine (Faltis, *Monatsh.*, 1910, **31**, 563). Since the latter acid can only be (III), the opening of the anhydride ring in our case (and in analogous ones) takes place in the neighbourhood of the methoxy-groups: the acid is converted into alizarin dimethyl ether by concentrated sulphuric acid at 30°. The analogous condensation

of hemipinic anhydride and benzene under the influence of aluminium chloride gives a hydroxymethoxybenzoylbenzoic acid (Lagodzinski, *Ber.*, 1895, **28**, 1427).

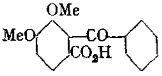
Hemipinic anhydride reacted with the Grignard derivatives of α-bromonaphthalene and of 2-bromo-6-methoxynaphthalene to give 2-α-naphthoyl- and 2-(6′-methoxy-2′-naphthoyl)-3 : 4-dimethoxybenzoic acid respectively. The former was converted by concentrated sulphuric acid into 1 : 2-dimethoxy-7 : 8-benzanthraquinone.



(I.)



(II.)



(III.)

EXPERIMENTAL.

Phthalic Anhydride and Naphthyl Methyl Ethers.—The anhydride (1 mol.) and the ether (1 mol.) were kept in benzene solution in presence of anhydrous aluminium chloride for 24 hours at room temperature. The product from the α-compound was *o*-(4′-methoxy-1′-naphthoyl)-benzoic acid, m. p. 194° (Cohn, *loc. cit.*; Schulenberg, *Ber.*, 1920, **53**, 1445; Fieser and Dietz, *loc. cit.*). β-Naphthyl methyl ether gave a greenish powder, which crystallised from butyl acetate in quartz-like crystals, m. p. 198°, of *o*-(2′-methoxy-1′-naphthoyl)benzoic acid (Found: OMe, 10·4. Calc.: OMe, 10·1%).

Phthalic Anhydride and 1 : 5-*Dimethoxynaphthalene.*—The same procedure as above gave *o*-(1′ : 5′-dimethoxy-4′-naphthoyl)benzoic acid as a brown powder, which crystallised from glacial acetic acid and from xylene in small prisms, m. p. 263° [Found: C, 71·2; H, 4·8; OMe, 19·2. Calc. for $C_{18}H_{10}O_3(OMe)_2$: C, 71·4; H, 4·8; OMe, 18·6%]. On crystallisation from acetic anhydride, it gave yellow prismatic plates, m. p. 185°, of the 8′-acetyl compound (Found: C, 69·8; H, 5·1. Calc. for $C_{22}H_{18}O_6$: C, 70·0; H, 4·5%).

2-*Methoxy*-1-*naphthylmagnesium Bromide and Phthalic Anhydride.*—The reagent prepared from magnesium turnings (1·4 g.; 2 mols.), a few drops of methyl iodide, and 1-bromo-β-naphthyl methyl ether (6·8 g.) in ether reacted violently with phthalic anhydride (3·5 g.) in boiling benzene. After 2 hours' boiling, the product was treated with ice and dilute sulphuric acid, the ethereal layer extracted with sodium hydroxide solution, and the extract acidified. The oily acid solidified after some hours and then separated from butyl acetate in crystals, m.p. 198°, undepressed by *o*-(2′-methoxy-1′-naphthoyl)benzoic acid (above). Concentrated sulphuric acid produced a red-brown solution, changing to violet.

Naphthalene-2 : 3-*dicarboxylic Anhydride and Pyrogallol Trimethyl Ether.*—The anhydride (4 g.), the ether (3·4 g.), and aluminium chloride (2·7 g.) were kept in carbon disulphide (50 c.c.) at room temperature for 24 hours, and then boiled for 2 hours. The acid product was dissolved in hot 90% acetic acid; naphthalene-2 : 3-dicarboxylic acid, m.p. 241° (decomp.), separated on cooling, followed, after dilution with water, by 3-(4′-*hydroxy*-2′ : 3′-*dimethoxybenzoyl*)-2-*naphthoic acid* (I), which crystallised from 50% acetic acid in needles, m.p. 245°, in poor yield (Found: C, 68·2; H, 4·8; OMe, 17·5. Calc. for $C_{20}H_{16}O_6$: C, 68·2; H, 4·5; OMe, 17·6%). The sulphuric acid colour reaction is reddish-violet.

6-(4′-Hydroxy-2′ : 3′-dimethoxybenzoyl)-2 : 3-dimethoxybenzoic acid (II), obtained similarly from hemipinic anhydride and pyrogallol trimethyl ether, formed prisms, m. p. 194—195°, from 50% acetic acid (Found: C, 59·6; H, 5·3; OMe, 34·9. Calc. for $C_{18}H_{18}O_8$: C, 59·7; H, 5·0; OMe, 34·3%).

4-*Lithio*-1 : 2 : 3-*trimethoxybenzene and Phthalic Anhydride.*—13·5 G. of 4-iodo-1 : 2 : 3-trimethoxybenzene and 0·8 g. of lithium were shaken with 200 c.c. of ether in a Schlenk tube for 8 days. The precipitated lithium compound was introduced (in a nitrogen atmosphere) into a boiling solution of 6·6 g. of phthalic anhydride in benzene. The reaction was rather violent and was completed by 2 hours' boiling. The usual treatment gave *o*-(2′ : 3′ : 4′-trimethoxybenzoyl)benzoic acid, which was triturated with glacial acetic acid and recrystallised from 25% acetic acid; it formed stout prisms, m. p. 196°, giving a brown-yellow colour reaction with concentrated sulphuric acid (Found: C, 64·5; H, 5·1. Calc. for $C_{17}H_{16}O_6$: C, 64·6; H, 5·1%). The product, m. p. 169°, obtained by Bentley and Weizmann (J., 1908, **93**, 436) in the analogous aluminium chloride condensation was certainly partly demethylated (compare the above-mentioned experiments).

Phenylmagnesium Bromide and Hemipinic Anhydride.—The Grignard solution (magnesium, 0·3 g.; bromobenzene, 1·1 c.c.) was introduced into a boiling suspension of hemipinic anhydride (2 g.) in benzene. The yellowish crystalline product was treated with cold sulphuric acid and extracted with alkali. The alkaline solution, which, as in all these experiments, exhibited a strong greenish-yellow fluorescence, was acidified, and the resinous 2-benzoyl-3 : 4-dimethoxybenzoic acid (III) triturated with and recrystallised from 50% acetic acid; it formed prisms, m. p. 192°, which gave a purple colour reaction with sulphuric acid. *Cyclisation.* 0·2 G. was treated with sulphuric acid (5 c.c.) at 30° for 24 hours. The mass was poured into water, and the yellow precipitate centrifuged off aud freed from unchanged acid by washing with sodium carbonate solution. On crystallisation from butyl acetate, a small quantity of orange-red needles, m. p. 192°, was obtained, which gave a stable red colour with concentrated sulphuric acid and could not be identified; then silky yellow needles of alizarin 1 : 2-dimethyl ether, m. p. 209—210°, separated.

α-Naphthylmagnesium Bromide and Hemipinic Anhydride.—From α-bromonaphthalene (1·5 c.c.), 2-α-naphthoyl-3 : 4-dimethoxybenzoic acid was obtained. It separated from 60% acetic acid in lancet-shaped crystals, m. p. 223° (slight decomp.), giving a blue-green, then dark blue, colour with sulphuric acid (Found : C, 71·1; H, 5·0. Calc. for $C_{20}H_{16}O_5$: C, 71·4; H, 4·8%). When treated with concentrated sulphuric acid at 30° for 48 hours, it gave red needles, m. p. 240°, of 1 : 2-dimethoxy-7 : 8-benzanthraqninone, which were recrystallised from glacial acetic acid or butyl acetate (Found : C, 75·5; H, 4·7. Calc. for $C_{20}H_{14}O_4$: C, 75·5; H, 4·5%).

2-(6′-Methoxy-β-naphthoyl)-3 : 4-dimethoxybenzoic acid, similarly obtained from the magnesium derivative of 2-bromo-6-methoxynaphthalene (2·4 g.), was triturated with 50% acetic acid and recrystallised from butyl acetate. The acid, which gives a dark green, then dark blue colour reaction with sulphuric acid, is dimorphous, crystallising in octahedra, m. p. 237°, or needles, m. p. 240° (after sintering) (Found : C, 68·8; H, 5·2. Calc. for $C_{21}H_{18}O_6$: C, 68·8; H, 4·9%).

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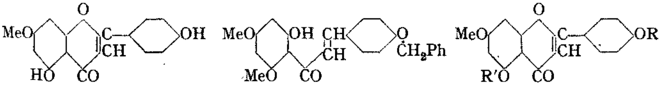
124. *Synthetical Experiments in the Chromone Group. Part XIX. A Synthesis of Genkwanin.*

By Harbhajan S. Mahal and Krishnasami Venkataraman.

Nakao and Tseng (*J. Pharm. Soc. Japan*, 1932, No. 602, 343; 1933, No. 608, 905) isolated genkwanin from the Chinese drug " yuen-hua " and proposed the structure (I) for it : this was confirmed by Tseng (*ibid.*, 1935, No. 636, 30) by its synthesis from phloracetophenone



(I.) (II.) (III.)

and *p*-benzyloxybenzoic anhydride, followed by partial methylation and debenzylation. We have synthesised genkwanin as follows: *2-Hydroxy-4′-benzyloxy-4 : 6-dimethoxychalkone* (II) was oxidised by means of selenium dioxide (Mahal, Rai, and Venkataraman, J., 1935, 866) to the *flavone* (III; R = CH_2Ph, R′ = Me); debenzylation with hydrochloric acid in acetic acid gave *genkwanin 5-methyl* ether (III; R = H, R′ = Me), which was converted into genkwanin (I) by partial demethylation with aluminium chloride (Gulati and Venkataraman, this vol., p. 267).

Although ω-benzoyl-2 : 4 : 6-trimethoxyacetophenone could be demethylated in the 2-position and cyclised to chrysin dimethyl ether in one operation by treatment with aluminium chloride in nitrobenzene, a similar reaction with the 4′-*benzyloxy*-analogue gave 5 : 7-dimethoxy-4′-benzyloxyflavone in very poor yield.

Interaction of alcoholic potash and the dibromide of the *O*-acetyl derivative of the

chalkone (II) produced the corresponding coumaranone, as indicated by the colour reactions, and not the flavone (III).

Experimental.

ω-4′-*Benzyloxybenzoyl*-2 : 4 : 6-*trimethoxyacetophenone*.—A mixture of 2 : 4 : 6-trimethoxyacetophenone (3 g.), methyl *p*-benzyloxybenzoate (7·2 g.), and sodium dust (0·5 g.) was heated at 120° for 3 hours. After treatment with ice-water the liquid was filtered and saturated with carbon dioxide. The precipitated *diketone* crystallised from alcohol in yellow needles (1·1 g.), m. p. 101—102°, which gave a dark red colour with alcoholic ferric chloride (Found *: C, 71·5; H, 5·8. $C_{25}H_{24}O_6$ requires C, 71·4; H, 5·7%).

2-*Hydroxy*-4′-*benzyloxy*-4 : 6-*dimethoxychalkone* (II).—2-Hydroxy-4 : 6-dimethoxyacetophenone (Gulati and Venkataraman, *loc. cit.*, 7 g.) and *p*-benzyloxybenzaldehyde (9 g.), by treatment with alcoholic caustic soda, gave the *chalkone*, which crystallised from glacial acetic acid in golden-yellow needles (7 g.), m. p. 159° (Found: C, 73·6; H, 5·7. $C_{24}H_{22}O_5$ requires C, 73·8; H, 5·6%), and developed a deep red colour with alcoholic ferric chloride. The *acetyl* derivative, stout colourless needles from alcohol, melted at 105° (Found: C, 72·0; H, 5·7. $C_{26}H_{24}O_6$ requires C, 72·2; H, 5·6%).

4′-*Benzyloxy*-5 : 7-*dimethoxyflavone* (III; R = CH_2Ph, R′ = Me).—A mixture of (II) (7 g.), selenium dioxide (7 g.), and amyl alcohol (100 c.c.) was refluxed for 12 hours, the selenium removed and washed with ether, and the combined solutions extracted with 20% aqueous caustic soda; the precipitated solid was collected (3·5 g.), and removal of the solvents from the ether–amyl alcohol layer by warming on the water-bath, followed by steam distillation, gave more (1·5 g.) of the same substance. Two crystallisations of the combined product from alcohol gave orange-yellow needles, m. p. 178°, exhibiting no ferric chloride reaction (Found: C, 74·3; H, 5·4. $C_{24}H_{20}O_5$ requires C, 74·2; H, 5·1%).

Genkwanin 5-Methyl Ether (III; R = H, R′ = Me).—The debenzylated substance obtained from 3·5 g. of the benzyl ether crystallised from alcohol in pale yellow needles (1·6 g.), m. p. 298° (Found *: C, 68·2; H, 4·9. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%), which gave a pale brown ferric chloride coloration. The *acetyl* derivative crystallised from alcohol in colourless needles, m. p. 220° (Found *: C, 66·6; H, 4·5. $C_{19}H_{16}O_6$ requires C, 67·0; H, 4·7%).

Genkwanin (I).—The above methyl ether (0·5 g.), aluminium chloride (0·6 g.), and nitrobenzene (3 c.c.) were heated on a boiling water-bath for 1 hour, ice and hydrochloric acid added, the nitrobenzene removed with steam, and the residue acetylated by means of acetic anhydride and pyridine. The fine colourless needles (0·2 g., from alcohol) of the acetate had m. p. 197—198°, undepressed by the acetate of natural genkwanin (Found *: C, 64·8; H, 4·2. Calc. for $C_{20}H_{16}O_7$: C, 65·2; H, 4·3%). Hydrolysis of the acetate, by warming with 50% hydrochloric acid on the water-bath for a few minutes, and crystallisation from aqueous acetone gave bright yellow needles, m. p. and mixed m. p. with natural genkwanin, 285—286° (Found *: C, 67·9; H, 4·6. Calc. for $C_{16}H_{12}O_5$: C, 67·6; H, 4·2%). The colour reactions also were identical.

The analyses marked * were carried out by Dr. Ing. A. Schoeller. We are grateful to Principal T. S. Wheeler of the Royal Institute of Science for facilities in his laboratory afforded to one of us (H. S. M.), who wishes also to thank the Lady Tata Memorial Trust for a scholarship. We are deeply indebted to Dr. Kwong-fong Tseng for specimens of genkwanin and diacetylgenkwanin.

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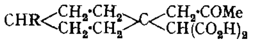
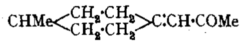
125. *Studies in Keto-lactol Tautomerism. Part V. The Influence of Methyl*cyclo*hexane Rings on the Tautomerism of δ-Ketonic Acids.*

By Muhammad Qudrat-i-Khuda and Ashutosh Mukherji.

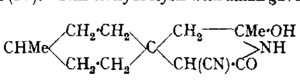
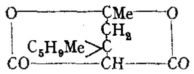
It has been suggested (Qudrat-i-Khuda, J., 1929, 713) that the ready conversion of 1-acetonyl*cyclo*hexane-1-malonic acid (I, R = H) into the lactol (68% on melting) could be explained by the deflection of the carbon tetrahedral angle due to the *cyclo*hexane ring, in accordance with the Thorpe–Ingold theory. The difference between the *cyclo*pentane and the *gem*-dimethyl analogue of the acid (I, R = H), which should behave in the same

way according to this theory, may be attributable to some additional factor. Recent results have been interpreted on the assumption of a multiplanar structure of substituted *cyclo*hexane rings (compare Qudrat-i-Khuda, *J. Indian Chem. Soc.*, **1933**, **8**, 277), and the lactol change in homologues of the acid (I, R = H) containing such rings has therefore been investigated. The results, reported below, do not however permit a definite conclusion to be drawn.

For the preparation of the acid (I, R = Me), the unsaturated ketone (II) was required. It was found, however, that a mixture of this with its Δ^{β}-isomeride could be employed and that this could be readily prepared in quantity by the method used by Jupp, Kon, and Lockton (J., 1928, 1638) for the preparation of the unsubstituted compound.

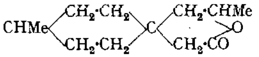
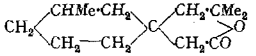
(I.)   (II.)

4-Methyl*cyclo*hexenylacetone was condensed with sodiocyanoacetamide to give the *imido*-compound (III), which was easily hydrolysed by concentrated hydrochloric acid to the *dilactone* (IV). This on hydrolysis with alkali gave the dibasic acid (I, R = Me), which lactonised slowly under laboratory conditions; its *silver* salt was analysed.

(III.)   (IV.)

1-*Acetonyl*-4-*methyl*cyclo*hexane*-1-*acetic acid* was obtained in small quantity from the product of hydrolysis of the imide (III) and in some amount, together with the dilactone (IV), on decomposition of the freshly prepared dibasic acid by heat. Its *ethyl* ester, prepared by esterification of the acid and also from ethyl hydrogen 4-methyl*cyclo*hexane-1 : 1-diacetate through the acid chloride and methylzinc iodide, had the normal structure and yielded a *semicarbazone*. The acid yielded the *lactone* (V) on reduction with sodium and alcohol.

The imido-compound (III) on hydrolysis with caustic potash yielded a mixture of 82% of the acid (I, R = Me) and 18% of the dilactone (IV). The mixture, heated above its melting point, gave 58% of the dilactone and 35·7% of 1-acetonyl-4-methyl*cyclo*hexane-1-acetic acid.

(V.)   (VI.)

3-Methyl*cyclo*hexenylacetone condensed fairly well with cyanoacetamide in presence of sodium ethoxide. The *imido*-compound (III, with Me in position 3 instead of 4) behaved similarly to other imido-compounds. 1-Acetonyl-3-methyl*cyclo*hexane-1-malonic acid could be obtained only in an impure condition by hydrolysis of the corresponding *dilactone* (as IV), because it underwent extensive lactonisation on standing. The freshly prepared acid, when heated above its melting point, decomposed with the production of a mixture of 67% of the dilactone and 25% of 1-*acetonyl*-3-*methyl*cyclo*hexane*-1-*acetic acid*. The *ethyl* ester of the latter acid was prepared as before, and on hydrolysis yielded the acid in a fairly pure condition. The ester reacted with methylmagnesium iodide to give the *lactone* (VI), with sodium ethoxide it gave 3-*methylcyclo*hexane*spirocyclo*hexane-3' : 5'-*dione*, and on reduction it yielded the *lactone* (as V).

Much difficulty was experienced in preparing the corresponding unsaturated ketone from 2-methyl*cyclo*hexanone and the work is not yet complete.

Experimental.

4-*Methyl*cyclo*hexenylacetone*.—Acetoacetic ester (72 g.) was poured into a cold solution of sodium (11·5 g.) in absolute alcohol (160 c.c.), 4-methyl*cyclo*hexanone (56 g.) added, and the mixture heated on a water-bath for 26 hours, and again for 8 hours after addition of water (60

c.c.). Alcohol was then distilled off from a water-bath, and the remaining oil refluxed with concentrated hydrochloric acid (100 c.c.) for 1½ hours. The ketone, extracted from the cooled diluted product with ether, washed with sodium bicarbonate solution, and dried over calcium chloride, had b. p. 121—122°/40 mm. (yield, 60—70%) and gave a semicarbazone, m. p. 126° (Kon and Thakur, J., 1930, 2229). Iodometric estimation (Linstead and May, J., 1927, 2565) showed that it consisted of 30·3% of the Δ^{α}- and 69·7% of the Δ^{β}-isomeride.

4-*Methyl*cyclo*hexane*-1 : 4-spiro-2'-*hydroxy*-6'-*keto*-5'-*cyano*-2'-*methylpiperidine* (III).—A hot saturated alcoholic solution of cyanoacetamide (8·4 g.) was added to a solution of sodium (2·3 g.) in absolute alcohol (30 c.c.) and heated with the preceding ketone (15 g.) on a water-bath for 4—5 hours, the odour of ammonia then being perceptible. The alcohol was distilled off and the residue was cooled, dissolved in water, and extracted with ether to remove neutral products. Acidification of the aqueous solution with dilute hydrochloric acid gave the *imide* (III) (11·5 g.), which was crystallised from dilute methyl alcohol; it did not melt below 300° (Found: C, 66·5; H, 8·8. $C_{13}H_{20}O_2N_2$ requires C, 66·1; H, 8·5%).

Hydrolysis. The imido-compound (III) (10 g.) was heated with concentrated hydrochloric acid (100 c.c.) on a water-bath for 4 hours. The crystalline *dilactone* (IV) that separated on cooling was washed with water and recrystallised from dilute alcohol; m. p. 172° (Found: C, 65·2; H, 7·6. $C_{13}H_{18}O_4$ requires C, 65·5; H, 7·5%).

The dilactone (5 g.) was heated with 10% aqueous sodium hydroxide (50 c.c.) on a water-bath for 1½ hours, and the clear solution acidified at 0° with hydrochloric acid. The dibasic acid (I, R = Me), obtained as an oil, was isolated by means of ether and kept in a vacuum desiccator; after 3 weeks it had almost completely changed into the dilactone. The *silver* salt, obtained from the freshly prepared acid through the ammonium salt, was only slightly soluble in water (Found: Ag, 45·8. $C_{13}H_{18}O_6Ag_2$ requires Ag, 45·9%).

1-*Acetonyl*-4-*methyl*cyclo*hexane*-1-*acetic Acid*.—(1) The freshly prepared dibasic acid (I, R = Me) (5 g.) was heated at 170° for an hour and the residue was cooled, treated with cold dilute sodium bicarbonate solution, and shaken with ether (which extracted 3 g. of the dilactone, m. p. 172°). The aqueous solution on acidification deposited 1·8 g. of the monobasic acid as a thick syrup (Found for the *silver* salt: Ag, 33·5. $C_{12}H_{19}O_3Ag$ requires Ag, 33·8%), which gave a *semicarbazone* crystallising from alcohol in needles, m. p. 195° (decomp.) (Found: C, 58·5; H, 8·6. $C_{13}H_{23}O_3N_3$ requires C, 58·0; H, 8·5%).

(2) The anhydride (52 g.) obtained from 4-methyl*cyclo*hexane-1 : 1-diacetic acid (70 g.) (Wood and Thorpe, J., 1913, **103**, 1583), when boiled with ethyl alcohol (45 c.c.), yielded ethyl hydrogen 4-methyl*cyclo*hexane-1 : 1-diacetate (68 g.) as a thick syrup (Found for the insoluble *silver* salt: Ag, 31·1. $C_{13}H_{21}O_4Ag$ requires Ag, 31·0%). This acid ester (20 g.) was treated with thionyl chloride (25 c.c.), the excess of the latter removed under reduced pressure, and the acid chloride added to a solution of methylzinc iodide prepared from 43 g. of zinc–copper couple, 11 c.c. of dry ethyl acetate, 25 c.c. of dry methyl iodide, and 50 c.c. of sodium-dried benzene. The keto-ester was obtained as a mobile liquid, b. p. 163—165°/31 mm., the *semicarbazone* of which had m. p. 140° after crystallisation from dilute ethyl alcohol (Found: C, 60·8; H, 9·2. $C_{15}H_{27}O_3N_3$ requires C, 60·6; H, 9·1%). *Ethyl* 1-*acetonyl*-4-*methyl*cyclo*hexane*-1-*acetate* regenerated from the semicarbazone had b. p. 133°/3 mm., $d_{4°}^{30°}$ 0·99033, $n_D^{30°}$ 1·45781, $[R_L]_D$ 66·1 (calc., 66·3) (Found: C, 70·2; H, 9·9. $C_{14}H_{24}O_3$ requires C, 70·0; H, 10·0%) and on hydrolysis (20 g.) with caustic potash (9 g.) in water (9 c.c.) and rectified spirit (70 c.c.) gave, after 3 hours' heating, a liquid (14 g.), the semicarbazone of which, m. p. 195°, was identical with that described under (I). The *acid* regenerated from the semicarbazone was a thick syrup, b. p. 183°/6 mm. (Found: C, 68·2; H, 9·4. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·4%). The *methyl* ester, b. p. 120°/2 mm., was prepared from the acid and methyl-alcoholic hydrogen chloride at − 6° and then on a steam-bath (Found: C, 69·1; H, 9·7. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·7%); it gave a *semicarbazone* which crystallised from dilute alcohol in short needles, m. p. 155° (Found: C, 59·6; H, 9·0. $C_{14}H_{25}O_3N_3$ requires C, 57·3; H, 8·8%).

Reduction. To a mixture of absolute alcohol (25 c.c.) and 1-acetonyl-4-methyl*cyclo*hexane-1-acetic acid (10 g.) heated at 110° under reflux, sodium (9 g.) was gradually added, followed by alcohol (3 × 25 c.c.) at 15-minute intervals. The alcohol was removed in steam, the hot alkaline solution acidified with hydrochloric acid, and the oily product extracted with ether, washed with sodium bicarbonate solution, dried, and distilled, yielding the *lactone* (V) as a mobile liquid, b. p. 142°/3 mm., $d_{4°}^{30·7°}$ 1·00126, $n_D^{30·7°}$ 1·47165, $[R_L]_D$ 54·78 (calc., 54·87) (Found: C, 74·0; H, 9·7. $C_{12}H_{20}O_2$ requires C, 73·45; H, 10·2%).

3-*Methyl*cyclo*hexenylacetone*.—Prepared from 3-methyl*cyclo*hexanone (56 g.) and acetoacetic ester (72 g.) by the method described for the 4-methyl compound, the ketone, b. p. 93—

94°/12 mm., consisting of 31% of the Δ^{α}- and 69% of the Δ^{β}-isomeride, was obtained in 50—55% yield; it gave a semicarbazone, m. p. 188—189° (Kon and Thakur, *loc. cit.*).

The Imido-compound (as III).—Condensation of 3-methyl*cyclo*hexenylacetone (7·5 g. and cyanoacetamide (4·2 g.) yielded the *imido*-compound in 58% yield; m. p. above 300° after crystallisation from dilute methyl alcohol (Found: C, 65·5; H, 8·4%).

Hydrolysis. (1) The imido-compound (10 g.), heated with concentrated hydrochloric acid (100 c.c.) on the water-bath for 4 hours, gave the *dilactone* (as IV), m. p. 144° after crystallisation from dilute ethyl alcohol (Found: C, 65·4; H, 7·5%). The acid mother-liquor gave an oily product, which was completely soluble in sodium carbonate solution and formed a semicarbazone, m. p. 212°, identical with that of 1-acetonyl-3-methyl*cyclo*hexane-1-acetic acid (below).

(2) The imido-compound (10 g.) was heated with caustic potash (10 g.) in water (50 c.c.) on a sand-bath for 30 hours. The product was a mixture of the dilactone (as IV) and 1-acetonyl-3-methyl*cyclo*hexane-1-malonic acid; after it had been kept for a fortnight in a vacuum desiccator, it contained 80% of the dilactone. The *silver* salt of the acid was a white amorphous mass (Found: Ag, 45·9%).

The dilactone (4 g.) was hydrolysed with 10% caustic potash solution (40 c.c.) and the dibasic acid produced was extracted with ether (yield 3·5 g.). The freshly prepared acid (5·94 g.) was heated at 160—164° till the evolution of carbon dioxide ceased; the cooled mass was extracted with sodium carbonate solution, 4·02 g. of the dilactone and 1·5 g. of 1-acetonyl-3-methyl*cyclo*hexane-1-acetic acid being obtained. The semicarbazone, m. p. 212°, of this acid was identical with that of the synthetic acid (below).

*1-Acetonyl-3-methyl*cyclo*hexane-1-acetic Acid.*—3-Methyl*cyclo*hexane-1 : 1-diacetic anhydride (64 g.) was heated with absolute alcohol (40 c.c.) on a water-bath for 6 hours. The acid ester obtained was a thick syrup (70 g.); it formed an amorphous *silver* salt insoluble in water (Found: Ag, 30·8%). The ester (20 g.) was converted by thionyl chloride into the acid chloride, which was treated with methylzinc iodide. The *ethyl* 1-*acetonyl*-3-*methyl*cyclo*hexane*-1-*acetate* (17 g.) obtained had b. p. 175—178°/35 mm. and gave a *semicarbazone*, m. p. 105° (decomp.) after crystallisation from benzene–petroleum (Found: C, 60·1; H, 9·5%). The keto-ester regenerated from the semicarbazone had b. p. 129°/5 mm., $d_{4°}^{30·6°}$ 0·986547, $n_{D}^{30·6°}$ 1·45710, $[R_L]_D$ 66·27 (Found: C, 70·0; H, 9·4%). By internal Dieckmann condensation in presence of sodium ethoxide it yielded 3-methyl*cyclo*hexane*spirocyclo*hexane-3′ : 5′-dione, m. p. 137° after crystallisation from benzene–light petroleum (Kon and Thakur, *loc. cit.*).

Hydrolysis of the keto-ester (20 g.) with potassium hydroxide (10 g.) in alcoholic solution gave the acid as a thick syrup (15 g.), the *semicarbazone* of which crystallised in needles, m. p. 212° (Found: C, 58·0; H, 8·7%). The keto-acid regenerated from the semicarbazone had b. p. 161°/2 mm. (Found: C, 67·5; H, 9·6%). The *methyl* ester, prepared with methyl-alcoholic hydrogen chloride, had b. p. 135—136°/13 mm. (Found: C, 68·8; H, 9·7%) and formed a *semicarbazone*, m. p. 162° (decomp.) after crystallisation from dilute methyl alcohol (Found: C, 59·4; H, 8·9%).

The Grignard reagent prepared from magnesium (2 g.), methyl iodide (7 c.c.), and ether (25 c.c.) was added slowly to ethyl 1-acetonyl-3-methyl*cyclo*hexane-1-acetate (8 g.) in ether (50 c.c.) cooled in a freezing mixture. After being left at the ordinary temperature for 15 minutes, the product was decomposed with ice and dilute sulphuric acid and the oil that separated was extracted with ether, washed, and distilled under reduced pressure, yielding the *lactone* (VI), b. p. 159°/10 mm., $d_{4°}^{30·5°}$ 1·00072, $n_{D}^{30·5°}$ 1·46566, $[R_L]_D$ 58·1 (calc., 59·5) (Found: C, 73·9; H, 10·4. $C_{13}H_{22}O_2$ requires C, 74·2; H, 10·4%).

Reduction of the keto-acid (10 g.) with sodium and alcohol under the conditions employed in the previous case produced the *lactone* (as V) (1·5 g.), b. p. 187°/4 mm., $d_{4°}^{29·8°}$ 1·01913, $n_{D}^{29·8°}$ 1·47796, $[R_L]_D$ 54·4 (Found: C, 73·1; H, 9·6%).

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126. *Electrolytic Reduction of Organic Compounds. Part II. Catalytic Hydrogenation of Sorbic Acid at Prepared Cathodes of Nickel and Platinum.*

By Elias Isaacs and Christopher L. Wilson.

Polished cathodes of nickel and platinum will not reduce sorbic acid (Isaacs and Wilson, this vol., p. 204), but it is now recorded that the electrodeposition of spongy nickel or platinum-black on these cathodes converts them into efficient reducing agents. By employing the technique already described (*idem, ibid.*) the products of reduction have been analysed. In the following table, the results of typical experiments in aqueous media, each involving the partial reduction of 20 g. of sorbic acid, are summarised.

Reduction of sorbic acid at prepared nickel and platinum cathodes.

		Components of reduction product (%).			
		n-Hexenoic acids.			Unchanged
Cathode.	Medium.	Δ^{α}-.	Δ^{β}- + Δ^{γ}-.	*n*-Hexoic acid.	sorbic acid (g.).
Ni	70% HOAc	18·9	18·3	62·8	4·1
	N-NaOH	26·6	17·2	56·2	5·0
Pt	70% HOAc	45·9	5·2	48·9	11·6
	N-NaOH	Very little reduction.			

Prolongation of the reduction leads to an increase in the amount of hexoic acid, and it is apparent that the course of reduction at these cathodes contrasts sharply with that pursued at other metals. The latter produce mixtures of only Δ^{β}- and Δ^{γ}-*n*-hexenoic acids (*idem, ibid.*), and since the conditions of all our electrolytic experiments have been the same, the absence of Δ^{α}-*n*-hexenoic acid (and its anticipated reduction product, hexoic acid) indicates that in the experiments now described this acid cannot arise by prototropic isomerisation of the Δ^{β}-acid.

Farmer and Hughes (J., 1934, 1932) observed the production of Δ^{α}-*n*-hexenoic and *n*-hexoic acid during the partial hydrogenation of sorbic acid under the influence of nickel (Raney's catalyst). It appears, therefore, that a spongy nickel cathode reduces by a process which is essentially catalytic. A platinised platinum cathode behaves similarly, but comparison with the behaviour of hydrogen in the presence of platinum-black is not immediately possible; considerable uncertainty has attached to the exact course of this reaction (*idem*, J., 1934, 304; Ingold and Shah, J., 1933, 885). Consequently, we have made special experiments, and, using the analytical technique already referred to, have ascertained the products of the 50% hydrogenation of sorbic acid in alcoholic solution. Four different samples of Adams's catalyst were employed, the relative activities of which may be estimated from the times taken for the absorption at a constant rate of shaking; these are given in col. 2 of the following table of results.

Partial catalytic reduction of sorbic acid in presence of Adams's catalyst.

		Composition of reduction product (%).		
Catalyst	Duration of	*n*-Hexenoic acids.		
sample.	shaking (mins.).	Δ^{α}-.	Δ^{β}- + Δ^{γ}-.	*n*-Hexoic acid.
1	90	31·3	5·5	63·2
2	90	38·0	6·8	55·2
3	33	40·7	6·5	52·8
4	28	43·6	7·1	49·3

If we may assume that the nature of the solvent does not seriously influence the results (cf. Farmer and Hughes, J., 1934, 1930), these figures, which agree qualitatively with those given by these authors (J., 1934, 304), complete the analogy between catalytic hydrogenation and the behaviour of the prepared cathodes. In conformity with this conclusion, aliphatic unsaturated acids possessing a double bond in various positions (not only αβ-) relative to the carboxyl group have been reduced at a spongy nickel cathode (Pomilio, *Z. Elektrochem.*, 1915, **21**, 444), phenol has given *cyclo*hexanol at a platinised platinum cathode

(Bancroft and George, *Trans. Amer. Electrochem. Soc.*, 1930, **57**, 399), and phenanthrene has been partly hydrogenated at a cathode of palladised platinum (Breteau, *Bull. Soc. chim.*, 1911, **9**, 769). In contrast, it is to be expected that the carbonyl group, which is notoriously resistant to catalytic methods, can be reduced at smooth but not at platinised platinum as Müller has shown (*Z. Elektrochem.*, 1910, **16**, 236).

By acting as a reversible hydrogen electrode in aqueous and alcoholic solution, a particle of active catalyst in such a medium in the presence of hydrogen will have a potential approximating to that of a prepared cathode evolving hydrogen at a very small current density. It may therefore reasonably be assumed that the essential mechanism of both processes is the same. In non-ionising media and in the vapour phase, catalytic reduction doubtless proceeds through electrically neutral intermediates. On the other hand, it is now generally accepted that with non-transition metals and ionising media the reaction is ionic. Our future experiments will endeavour to define the limits of these two mechanisms.

EXPERIMENTAL.

Hydrogenation of Sorbic Acid with Adams's Catalyst.—Sorbic acid (28 g.) in alcohol (150 c.c., 95%) and platinum catalyst (0·1 g.) were shaken with hydrogen until approximately 1 mol. had been absorbed. After evaporation of the solvent, the residue was boiled with petroleum (200 c.c., b. p. 60—80°), cooled to 0°, the solution filtered from separated sorbic acid and evaporated, and the residue distilled from a fractionating Claisen flask at a fraction of a mm. pressure and a rate not exceeding 2 drops per minute. A clean separation from sorbic acid was thus obtained. Towards the end of this distillation, Δ^{α}-*n*-hexenoic acid usually solidified in the condenser and was identified by m. p. and mixed m. p. with an authentic specimen (cf. Farmer and Hughes, J., 1934, 305).

Redistillation of the reduction product, which confirmed the absence of sorbic acid, was carried out before analysis by the halogen absorption method already described in detail (Isaacs and Wilson, *loc. cit.*). In this way Δ^{α}- and (Δ^{β} + Δ^{γ})-hexenoic and hexoic acids were estimated. In addition, hexoic acid was isolated by adding excess of bromine to the reduction product and distilling it. The first fraction was converted into the amide and identified by m. p. and mixed m. p. with an authentic specimen.

Stability of Δ^{α}-n-Hexenoic Acid towards Platinum-black.—*cyclo*Hexene in the presence of palladium at 35° has been shown to give a mixture of benzene and *cyclo*hexane (Zelinski and Paulov, *Ber.*, 1933, **66**, 1420); it was considered feasible that a similar change might occur with Δ^{α}-*n*-hexenoic acid in the presence of highly active platinum-black. In this way the disagreement which has existed in the literature might have been explained.

Δ^{α}-*n*-Hexenoic acid (11·4 g.), platinum oxide (0·1 g.), and alcohol (100 c.c.) were shaken in a securely stoppered bottle (300 c.c.) filled initially with hydrogen. The platinum oxide was rapidly reduced. After 17 hours' shaking, the product was distilled, but gave no trace of sorbic acid.

Behaviour of Hexoic Acid in the Presence of Platinum-black and an Unsaturated Substance.—Farmer and Galley (J., 1933, 691) have stated that, although Δ^{α}-*n*-hexenoic acid is hydrogenated more rapidly than allyl alcohol, the reverse holds true in a mixture of these substances. This result may have been due to the instability of hexoic acid in the presence of a highly active catalyst and allyl alcohol. Allyl alcohol (7·8 g.), hexoic acid (12·6 g.), and platinum oxide (0·1 g.) in alcohol (20 c.c.) were shaken in a bottle with hydrogen (50 c.c.) and subsequently for 12 hours. No trace of sorbic or Δ^{α}-*n*-hexenoic acid could be detected in the product.

Details of Catalytic Reductions.—In each case, the acids in the class denoted by (*a*) were isolated, and those in (*b*) were titrated. *Expt.* 1. Absorption was complete in 90 minutes. Recovered material on distillation gave: (*a*) sorbic acid (7·25 g.) and Δ^{α}-hexenoic acid (3·76 g.); (*b*) hexoic acid (11·13 g.), Δ^{α}- (1·74 g.) and Δ^{β}- + Δ^{γ}-hexenoic acids (0·97 g.).

Expt. 2. Absorption complete in 90 minutes. Recovered material consisted of: (*a*) sorbic acid (10·75 g.) and Δ^{α}-hexenoic acid (1·25 g.); (*b*) hexoic acid (7·84 g.), Δ^{α}- (4·15 g.) and Δ^{β}- + Δ^{γ}-hexenoic acids (0·96 g.).

Expt. 3. Absorption took 33 minutes, the catalyst being the sample, 16 months old at the time of this experiment, used by Ingold and Shah (*loc. cit.*). Recovered material: (*a*) sorbic acid (9·6 g.) and Δ^{α}-hexenoic acid (4·43 g.); (*b*) hexoic acid (8·88 g.), Δ^{α}- (2·40 g.) and Δ^{β}- + Δ^{γ}-hexenoic acids (1·09 g.).

Expt. 4. The catalyst was extremely active, 1 mol. of hydrogen being absorbed in 28 minutes.

Product: (*a*) sorbic acid (9·43 g.) and Δ^{α}-hexenoic acid (3·53 g.); (*b*) hexoic acid (8·38 g.), Δ^{α}- (3·88 g.) and Δ^{β}- + Δ^{γ}-hexenoic acids (1·21 g.).

The isolated samples of the Δ^{α}-acid had m. p. 32° and were shown by titration to contain, in addition, not more than 2% of the Δ^{β}- + Δ^{γ}-acids; the above figures are appropriately corrected.

Electrolytic Reductions.—Preparation of cathodes. Nickel. Pure nickel gauze (30 mesh) was coated with a substantial deposit of spongy nickel by electrolysis for 1—2 hours of an ammoniacal solution of nickel ammonium sulphate, the current being 8—9 amps./sq. dm. of gauze. After being thoroughly washed, the cathodes were preserved under distilled water.

Platinum. A revolving cylindrical gauze cathode (as used in electrochemical analysis) was coated with platinum-black by electrolysis of platinic chloride solution (3 g. in 100 c.c., with 0·02 g. of lead acetate).

Details of Reductions.—70% Aqueous acetic acid containing sodium acetate (0·5*M*) and *N*-sodium hydroxide were used as solvents for sorbic acid and the sodium salt respectively. The method has been previously described, and the symbols *B* and *J* have the same significance as before (Isaacs and Wilson, *loc. cit.*).

Expt. 1. *Nickel in acetic acid.* Sorbic acid (16 g.) was reduced with 35 amp.-hrs. of current (theoretical for dihydro-acid, 8 amp.-hrs.) and gave (*a*) sorbic acid (2·0 g.) and (*b*) a liquid, b. p. 101—102°/12 mm. (12·4 g.) (Found: *B*, 8·3; *J*, 8·4. Hexoic acid, 91·7; Δ^{α}, 0; Δ^{β} + Δ^{γ}, 8·3%). 11·5 G. of (*b*) were treated with excess of bromine for 24 hours and distilled, giving a liquid, b. p. 110—111°/19 mm. (9·8 g.), identified as hexoic acid by m. p., − 2° (Gartenmeister, *Annalen*, 1886, **233**, 277, gives m. p. − 2°), and formation of the amide, m. p. 98·5° (Robertson, J., 1919, **115**, 1220, gives 101°) (Found: C, 62·2; H, 11·3; N, 12·0. Calc.: C, 62·5; H, 11·4; N, 12·1%).

Expt. 2 (*as* 1). Sorbic acid (20 g.) was reduced at 1 amp. for 18 hours (theoretical for tetrahydro-acid, 20 hrs.) and gave (*a*) sorbic acid (13·9 g.) and (*b*) 13·9 g. of a liquid, b. p. 108—109°/17 mm. (Found: *B*, 37·2; *J*, 18·3. Hexoic acid, 62·8; Δ^{α}, 18·9; Δ^{β} + Δ^{γ}, 18·3%). Redistillation of (*b*) at a rate not exceeding 2 drops/min. and a pressure of less than 1 mm. gave, as last fraction, Δ^{α}-*hexenoic acid, m. p.* 32·2°; *mixed m. p. with authentic specimen* (m. p. 32·3°) 32·2°.

Expt. 3. *Nickel in alkaline solution.* Sorbic acid (20 g.) and 25 amp.-hrs. gave (*a*) sorbic acid (5·0 g.), (*b*) 13·6 g., b. p. 102—103°/11 mm. (Found: *B*, 43·8; *J*, 17·2. Hexoic acid, 56·2; Δ^{α}, 26·6; Δ^{β} + Δ^{γ}, 17·2%). Redistillation of (*b*) as above gave Δ^{α}-hexenoic acid, m. p. 32·0°, mixed m. p. 32·1°.

Expt. 4. *Platinum in acetic acid.* Reduction of sorbic acid (20 g.) for 24 amp.-hrs. gave (*a*) sorbic acid (11·6 g.) and (*b*) a liquid, b. p. 108—109°/17 mm. (6·5 g.) (Found: *B*, 51·1; *J*, 5·2. Hexoic acid, 48·9; Δ^{α}, 45·9; Δ^{β} + Δ^{γ}, 5·2). Redistillation gave 0·8 g. of Δ^{α}-hexenoic acid, m. p. 31·9°, mixed m. p. 32·0°.

Expt. 5. *Platinum in alkaline solution.* Preliminary experiments in the differential apparatus (Isaacs and Wilson, *loc. cit.*) showed very low efficiency; the experiments were not pursued.

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127. *Isomeric Forms of the Optically Active αγ-Dimethylallyl Alcohols.*

By H. W. J. Hills, J. Kenyon, and H. Phillips.

Unsaturated alcohols of the general formula CHR′:CH·CH(OH)·R″ undergo prototropic (CH_2R'·CH_2·CO·R″, Tiffeneau, *Bull. Soc. chim.*, 1907, **1**, 1209; Nomura, *ibid.*, 1925, **37**, 1245) and anionotropic changes [CHR′(OH)·CH:CHR″, Gillet, *Bull. Soc. chim. Belg.*, 1922, **31**, 366; Burton and Ingold, J., 1928, 904], indicating that under certain conditions the double bonds are activated. The effect of this activation on the optical properties of (+)-αγ-dimethylallyl alcohol is now described and discussed.

dl-αγ-Dimethylallyl hydrogen phthalate was resolved by recrystallisation of its brucine salt by Levene and Haller (*J. Biol. Chem.*, **1929**, **81**, 705), who isolated the (+)-hydrogen phthalic ester and the corresponding (+)-alcohol, but did not examine them in detail

polarimetrically. We have found that the maximum rotation of the (+)-hydrogen phthalic ester obtained from any such resolution is always $[\alpha]_{5461}$ + 30·2° (*c*, 5) in chloroform solution. In other solvents the rotatory powers of this ester (Table I) are not abnormal, and when plotted, they fall on a single characteristic diagram (Armstrong and Walker, *Proc. Roy. Soc.*, 1913, *A*, **88**, 388). The (−)-αγ-dimethylallyl hydrogen phthalate, $[\alpha]_{5461}$ − 29·4°, is obtained by the recrystallisation of its brucine salt, which separates from the concentrated mother-liquors from which the (+)-αγ-dimethylallyl hydrogen phthalate has been removed.

TABLE I.

Specific Rotatory Powers, $[\alpha]_{\lambda}^{15-20°}$, of (+)-αγ-Dimethylallyl Hydrogen Phthalate in various Solvents.

Solvent.	*c*.	$[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4359}$.	Solvent.	*c*.	$[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4359}$.
H_2O (Na salt)	10·0	+26·7°	+33·7°	+ 66·7°	C_5H_5N	10·0	+17·2°	+20·9°	+46·3°
	5·0	+23·0	+27·7	+ 57·5		5·0	+17·9	+21·7	+47·7
EtOH	10·0	+39·0	+48·5	+ 97·6		2·5	+19·2	+23·0	+49·4
	5·0	+38·3	+49·0	+ 97·6	CCl_4	10·0	+12·8	+15·9	+36·1
	2·5	+41·0	+49·2	+100·2	$CHCl_3$	10·0	+23·7	+29·4	+60·5
	1·25	+41·2	+52·0	+104·8		5·0	+23·9	+30·2	+62·5
Et_2O	10·0	+48·75	+46·7	+ 93·5		2·5	+25·4	+31·4	+63·4
	5·0	+40·5	+49·1	+ 95·0		1·25	+26·0	+32·0	+64·0
	2·5	+41·8	+50·0	+ 95·6	$C_2H_4Cl_2$	10·0	+22·3	+27·1	+57·1
$COMe_2$	10·0	+38·5	+47·1	+ 93·7		5·0	+23·2	+28·4	+60·9
	5·0	+39·0	+47·8	+ 93·0	$C_2H_4Br_2$	10·0	+21·0	+26·0	+53·6
	2·5	+45·0	+50·0	+ 94·6		5·0	+21·7	+26·0	+54·5
C_6H_6	10·0	+22·9	+27·7	+ 58·5		2·5	+22·0	+26·3	+55·0
	5·0	+24·0	+28·8	+ 60·0		1·25	+21·6	+26·4	+56·0
	2·5	+24·2	+30·1	+ 61·0	CS_2	10·0	+10·1	+10·3	+14·8
	1·25	+24·8	+30·4	+ 62·0		5·0	− 2·1	− 2·1	+ 1·0

When saponified by alkalis, the (+)-hydrogen phthalic ester gives (+)-αγ-dimethylallyl alcohol, the rotatory power of which varies, but is usually close to $[\alpha]_{5461}^{20°}$ + 0·84°. As shown in Table II, the rotatory power of this (+)-alcohol changes, and after about 2 months may eventually become lævorotatory to light of λ 5893 and 5461. Similarly, the optically impnre (−)-alcohol from the (−)-hydrogen phthalic ester ($[\alpha]_{5461}$ − 21·4° in chloroform) may decrease in lævorotatory power. The behaviour of the (+)- and the (−)-αγ-dimethylallyl alcohol is, however, erratic. A specimen of the (−)-hydrogen phthalic ester with $[\alpha]_{5461}$ − 6·0° in chloroform gave a (+)-alcohol with $\alpha_{5461}^{19°}$ + 0·10° (*l*, 1), which changed to $\alpha_{5461}^{19°}$ + 2·26° (*l*, 1) after 6 months and then gave a hydrogen phthalic ester with $[\alpha]_{5461}$ − 5·5°; after a further 3 months, the alcohol had $\alpha_{5461}^{19°}$ + 2·04° and gave a hydrogen phthalic ester with $[\alpha]_{5461}$ − 5·6°, from which on hydrolysis the alcohol was recovered with $\alpha_{5461}^{19°}$ + 1·0° (*l*, 1). Furthermore, some samples of the alcohols when freshly isolated from the hydrogen phthalic ester changed more rapidly than others: one sample changed from $\alpha_{5461}^{18°}$ + 0·83° to − 0·88° (*l*, 1) in 14 days, and another from $\alpha_{5461}^{18°}$ − 0·57° to + 0·35° in 1 day and to $\alpha_{5461}^{18°}$ + 4·48° in 131 days.

TABLE II.

The Mutarotation of (+)- and (−)-αγ-Dimethylallyl Alcohols.

(+)-Alcohol.

Time, days.	*t*.	a (*l*, 1). λ 5893.	λ 5461.	λ 4358.
0	19·6°	+0·23°	+0·46°	+1·82°
3	18·9	+0·24	+0·46	—
7	19·0	+0·16	+0·39	+1·72
10	16·0	+0·30	+0·53	+2·12
32	19·2	+0·02	+0·18	+1·27
53	19·0	−0·17	−0·02	—
123	24·0	−0·38	−0·36	—
		a (*l*, 2).		
0	20	+0·60	+1·02	+4·05
365	20	−0·41	−0·16	+1·90

(−)-Alcohol.

Time, days.	*t*.	a (*l*, 2). λ 5893.	λ 5461.	λ 4358.
0	18·9°	+0·05°	−0·68°	−1·40°
1	18·9	−0·53	−0·60	−2·58
2	19·3	−0·45	−0·66	−2·48
5	17·0	−0·50	−0·76	−2·51
8	19·0	−0·43	−0·76	−2·88
27	19·4	—	−0·43	—
48	19·5	−0·26	−0·38	−2·25
61	20·0	−0·21	−0·34	−2·23
69	22·0	−0·20	−0·19	−2·12
118	22·0	−0·02	−0·03	−1·77

A large quantity of (+)-αγ-dimethylallyl hydrogen phthalate was hydrolysed with aqueous sodium hydroxide, and the resulting (+)-αγ-dimethylallyl alcohol distilled, b. p. 120—121·5°, through a 6″ column: the middle fraction was collected in a clean polarimeter tube with sealed-on end-plates and closed by a well-fitting cork. The readings, taken from a short temperature–rotation curve, were $\alpha_{5893}^{20°}$ + 0·60°; $\alpha_{5461}^{20°}$ + 1·02°; $\alpha_{4358}^{20°}$ + 4·05° (*l*, 2). After a few weeks the rotatory power began to decrease, and after a year had reached $\alpha_{5893}^{20°}$ − 0·41°, $\alpha_{5461}^{20°}$ − 0·16°, $\alpha_{4358}^{20°}$ + 1·90° (*l*, 2). A portion of this alcohol yielded a hydrogen phthalic ester with $[\alpha]_{5893}$ + 19·6°; $[\alpha]_{5461}$ + 25·6° (*c*, 5·102; *l*, 2) in chloroform solution.

The erratic character of these changes is to some extent accounted for by the pronounced effect of temperature on the low rotatory power of the alcohol and by its anomalous rotatory dispersion (Table III).

The influence of temperature on the rotatory power of the (+)-alcohol is only partly due to *mutarotation*; *e.g.*, a (−)-alcohol with $[\alpha]_{5461}^{70°}$ − 1·33° (*l*, 0·5) had $[\alpha]_{5461}^{70°}$ − 1·61° (*l*, 0·5) after having been kept at 70° for 48 hours.

TABLE III.

Specific Rotatory Powers, $[\alpha]_\lambda^{t°}$, of (+)-αγ-Dimethylallyl Alcohol and its Derivatives (in the homogeneous state).

		20°.	30°.	40°.	50°.	60°.	70°.	80°.	90°.	100°.
					αγ-Dimethylallyl alcohol.					
$d_{4°}^{t°}$		0·8354	0·8270	0·8189	0·8106	0·8023	0·7941	0·7859	0·7776	0·7694
$[\alpha]_\lambda^{t°}$	λ 5893	+0·50°	−0·14°	−0·78°	−1·41°	−2·05°	−2·65°	−3·21°	−3·71°	−4·03°
	λ 5461	+0·84	+0·10	−0·61	−1·86	−2·12	−2·77	−3·41	−4·04	−4·61
	λ 4358	+3·04	+1·35	−0·12	−1·33	−2·37	−3·40	−4·20	−5·46	−6·37
					(−)-αγ-Dimethylallyl formate.					
$d_{4°}^{t°}$		0·8790	0·8693	0·8597	0·8500	0·8403	0·8305	0·8208	0·8110	0·8012
$[\alpha]_\lambda^{t°}$	λ 5893	−61·0	−59·8	−59·3	−58·9	−58·8	−58·5	−58·3	−58·0	—
	λ 5461	72·8	72·5	72·1	71·9	71·5	71·1	70·8	70·4	69·9
	λ 4358	129·0	128·3	127·9	127·3	126·9	126·2	125·4	125·0	124·9
					(−)-αγ-Dimethylallyl acetate.					
$d_{4°}^{t°}$		0·8980	0·8882	0·8788	0·8689	0·8591	0·8493	0·8395	0·8297	0·8199
$[\alpha]_\lambda^{t°}$	λ 5893	65·2	64·4	63·8	63·4	62·8	62·2	62·0	—	—
	λ 5461	76·1	75·3	74·5	73·7	73·2	72·9	72·5	72·0	71·2
	λ 4358	136·3	135·1	134·1	133·2	132·0	131·1	129·9	128·9	127·8
					(+)-αγ-Dimethylallyl benzoate.					
$d_{4°}^{t°}$		1·0149	1·0067	0·9984	0·9904	0·9820	0·9738	0·9656	0·9574	0·9492
$[\alpha]_\lambda^{t°}$	λ 5893	+20·6°	+20·7°	+20·8°	+20·9°	+21·0°	+21·1°	+21·2°	+21·3°	+21·4°
	λ 5461	26·5	26·4	26·2	26·2	26·3	26·1	25·9	25·9	25·8
	λ 4358	57·3	57·0	56·5	56·2	55·9	55·5	55·2	54·8	54·6
					(+)-αγ-Dimethylallyl o-*nitrobenzoate.*					
$d_{4°}^{t°}$		1·1424	1·1339	1·1254	1·1172	1·1087	1·1003	1·0913	1·0831	1·0743
$[\alpha]_\lambda^{t°}$	λ 5893	+22·4	+21·7	+21·1	+20·3	+19·65	+19·0	+18·3	+17·6	+16·9
	λ 5461	29·9	27·8	26·9	26·0	25·05	24·2	23·1	22·3	21·4
	λ 4358	77·1	74·2	71·5	69·0	66·6	64·2	62·5	60·8	59·2
					(+)-αγ-Dimethylallyl m-*nitrobenzoate.*					
$d_{4°}^{t°}$		1·1693	1·1609	1·1520	1·1432	1·1344	1·1259	1·1160	1·1082	1·0995
$[\alpha]_\lambda^{t°}$	λ 5893	+21·9	+21·4	+21·0	+20·8	+20·6	+20·2	+20·1	+20·0	+20·0
	λ 5461	27·0	26·5	26·0	25·6	25·4	24·9	24·7	24·4	24·2
	λ 4358	56·2	55·0	54·2	53·4	52·6	51·8	51·3	50·6	50·0
					(−)-Benzyl αγ-dimethylallyl ether.					
$d_{4°}^{t°}$		0·9740	0·9656	0·9574	0·9490	0·9403	0·9317	0·9230	0·9143	0·9057
$[\alpha]_\lambda^{t°}$	λ 5893	−38·4°	−38·0°	−37·5°	−36·9°	−36·2°	−35·6°	−35·1°	−34·6°	−34·0°
	λ 5461	45·6	44·9	44·3	43·6	43·0	42·3	41·7	40·9	40·2
	λ 4358	74·9	78·5	72·3	71·0	69·8	68·5	67·1	65·7	64·2

The rotatory power of the (+)-alcohol is very sensitive to the influence of solvents (Table IV). These rotatory powers, when plotted, give two distinct characteristic diagrams: those determined in water, ethyl alcohol, and carbon disulphide form one group, and those

in ether, benzene, pyridine, and chloroform another. No permanent mutarotation occurs in the solutions : the (+)-alcohol can be recovered from them without serious alteration in rotatory power.

TABLE IV.

Specific Rotatory Powers of (+)-αγ-Dimethylallyl Alcohol and its p-*Nitrobenzoate in Various Solvents.*

	(+)-*αγ-Dimethylallyl alcohol.*				(+)-*αγ-Dimethylallyl* p-*nitrobenzoate.*			
Solvent.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
H_2O	1·5	− 3·3°	− 4·3°	− 8·3°	—	—	—	—
EtOH	5·0	− 0·6	− 0·1	+ 1·6	—	—	—	—
CS_2	5·0	+ 1·2	+ 3·0	+ 8·4	5	+12·1°	+14·3°	+ 45·7°
Et_2O	5·0	− 5·8	− 7·0	− 9·4	5	+45·9	+57·3	—
C_6H_6	5·0	− 4·0	− 4·1	—	5	+37·6	+47·5	+115·0
C_5H_5N	5·0	+ 7·4	+ 8·9	+21·8	5	+35·5	+44·0	—
$CHCl_3$	10·0	−15·1	−17·5	−28·9	5	+45·0	+54·8	+127·3
	5·0	−15·4	−18·0	−32·6				

In sharp contrast to the parent (+)-alcohol, its esters with formic, acetic, benzoic, and *o*-, *m*-, and *p*-nitrobenzoic acids (like its hydrogen phthalic ester) are normal. Their rotatory powers are little influenced by temperature, they remain unchanged over long periods, and their dispersion is simple, since straight lines are obtained when $1/\alpha$ is plotted against λ^2. Similarly, benzyl αγ-dimethylallyl ether, prepared by the interaction of benzyl chloride and the potassio-derivative of the (+)-alcohol, also retains its rotatory power unchanged and exhibits simple rotatory dispersion.

The determined parachors of a number of specimens of (+)-, (−)-, and *dl*-αγ-dimethylallyl alcohols, prepared by the methods enumerated in Table V, are much smaller than those calculated from the atomic and structural parachors of either Sugden (" The Parachor and Valency," p. 38) or Mumford and (J.W.C.) Phillips, J., 1929, 2113. The differences between the observed and the calculated parachors are unlikely to be due to the presence of unforeseen impurities in these alcohols, since the (+)-alcohol has been converted into derivatives having parachors (Table VI) which are either very close to the values calculated for the open-chain, double-bond formulæ or deviate therefrom only slightly, the largest deviations being for the benzoate and the nitrobenzoates, all of which are somewhat unstable at their boiling points and are therefore difficult to obtain pure.

The parachors of allyl alcohol and some monosubstituted allyl alcohols have been determined (Table VII) : allyl alcohol has a normal parachor, but those of α- and γ-substituted alcohols are low.

TABLE V.

Observed Parachors of αγ-Dimethylallyl Alcohols.

Calc. for $CH_3\cdot CH\colon CH\cdot CH(OH)\cdot CH_3$:
{ Sugden .... 238·2
{ Mumford and Phillips .... 233·6

			Cyclic form, %.	
	t.	[*P*], obs.	S.	M. and P.
dl-Alcohol, from Grignard reaction	17—30°	226·7	99·5	82·0
dl-Alcohol, by hydrolysis of (+)-hydrogen phthalic ester with dil. H_2SO_4	21—31	230·5	64·0	2·0
dl-Alcohol, by hydrolysis of (+)-hydrogen phthalic ester with NaOAc soltn.	20—33	233·0	58·0	—
(+)-Alcohol, by hydrolysis of (+)-hydrogen phthalic ester with NaOH soltn.	20—25	228·3	83·5	49·0
(−)-Alcohol, by hydrolysis of (−)-hydrogen phthalic ester with NaOH soltn.	18—29	230·4	65·0	4·0
(+)- and (−)-Alcohols, by hydrolysis of (+)- and (−)-αγ-dimethylallyl chlorides .... (*a*)	20—30	229·2	80·0	29·5
(*b*)	20—30	227·4	90·0	68·0
(*c*)	20—30	226·0	100·0	87·0

The high parachor contribution of a double bond, 23·2 units (Sugden) or 19·0 units (Mumford and Phillips), suggests that the low observed parachors of the substituted allyl

TABLE VI.

Observed Parachors of Derivatives of (−)-αγ-Dimethylallyl Alcohol.

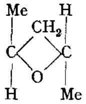
Derivative.	[*P*], obs.	[*P*], calc. S.	[*P*], calc. M. & P.	Derivative.	[*P*], obs.	[*P*], calc. S.	[*P*], calc. M. & P.
Formate	281·6	283·0	282·2	Methyl ether	277·2	277·2	276·0
Acetate	321·2	322·0	322·1	*n*-Butyl ether	393·8	396·2	396·0
Benzoate	450·5	455·9	455·8	Benzyl ether	446·1	450·1	450·6
o-Nitrobenzoate	506—509	514·5	513·9	Chloride	257·4	255·4	255·6
m-Nitrobenzoate	496·3	514·5	513·9				

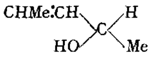
TABLE VII.

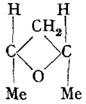
Observed Parachors of Allyl and Monosubstituted Allyl Alcohols.

Alcohol.	[*P*], obs.	Calc. (for open chain). S.	Calc. (for open chain). M. & P.	Cyclic form, %. S.	Cyclic form, %. M. & P.
Allyl	159·0	160·1	153·6	—	—
α-Ethylallyl	228·1	238·2	230·6	78	49
α-*n*-Butylallyl	305·9	316·2	310·6	85	100
γ-Phenylallyl	324·4	331·2	328·2	65	43

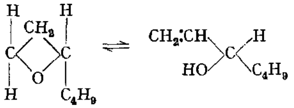
alcohols are due to isomerism during which their double bonds are lost. On this assumption, αγ-dimethylallyl alcohol (I), for example, might exist as an equilibrium mixture of labile open-chain and cyclic isomerides, two forms (II and III) of the latter being possible owing to *cis-trans*-isomerism. This hypothesis was adopted when we first described some


(II.)


(I.)


(III.)

of the properties of αγ-dimethylallyl alcohol (*Chem. and Ind.*, 1933, **52**, 660). Such isomerism might explain the anomalous rotatory dispersion of the alcohol, because (II) contains an additional centre of asymmetry and the alcohol would therefore contain two optically active alcohols, possibly of opposite rotations and with different dispersive powers. It might also account for the simple rotatory dispersion of *d*-α-*n*-butylallyl alcohol (Kenyon and Snellgrove, J., 1925, **127**, 1169), since this alcohol could give rise to only one cyclic isomeride without an additional centre of asymmetry:



Furthermore, isomerism of this type would be restricted to compounds containing a hydroxyl group, and hence the apparent homogeneity of the esters and ethers of αγ-dimethylallyl alcohol could be explained. This hypothesis would not, however, explain all our observations. For instance, the (+)-alcohol can be isolated from the optically pure hydrogen phthalic ester with a parachor of 228·3, indicating that it either contains 83·5% or 49% of the cyclic isomerides according as Sugden's or Mumford and Phillips's values are used for atomic and structural parachors. The (+)-alcohol would thus contain a certain proportion of isomeride (III), which, being internally compensated, would give rise to an optically inactive ester when re-esterified with phthalic anhydride. This should cause the (+)-alcohol to yield an optically impure hydrogen phthalic ester of low rotatory power. Experimentally, however, a freshly isolated alcohol with a parachor of 228·3 yielded a hydrogen phthalic ester possessing a rotatory power only 2° lower than that of the optically

pure ester. Similarly, the observed parachors of the α-substituted allyl alcohols suggest that these compounds contain a relatively large proportion of the cyclic isomerides, and these might be expected to yield a mixture of the α- and the γ-substituted allyl esters when re-esterified with acid anhydrides. Kenyon and Snellgrove (*loc. cit.*), however, recovered optically pure α-*n*-butylallyl alcohol from its formic ester which had been prepared by the use of the mixed anhydride of formic and acetic acids.

It might be argued that such evidence does not dispose of the hypothesis, since preferential esterification may cause the alcohols to yield only one hydrogen phthalic or formic ester; *e.g.*, the isomerisation of αγ-dimethylallyl alcohol may occur so as to favour the formation of isomeride (II), which would yield an optically pure hydrogen phthalic ester. Alternatively, for stereochemical reasons, preferential esterification of isomeride (II) may occur. Similarly, in the case of unsymmetrical alcohols, such as *d*-α-*n*-butylallyl alcohol, the cyclic form may react with acid anhydrides to produce exclusively either α- or β-substituted esters. In agreement with this view, Baudrenghien (*Bull. Soc. chim. Belg.*, 1922, **31**, 160) showed that α-methylallyl alcohol gave solely α-methylallyl acetate; further, although the parachor of α-phenylallyl alcohol (cinnamyl alcohol) suggests that it possibly contains a considerable proportion of a cyclic isomeride, it yields pure cinnamyl acetate when boiled with acetic anhydride (Burton and Ingold, *loc. cit.*).

Other observations have been made which are difficult to reconcile with the hypothesis of cyclic isomerisation. For example, when reduced, (—)-α-*n*-butylallyl alcohol yields optically pure (+)-ethyl-*n*-butylcarbinol (Levene and Haller, *J. Biol. Chem.*, 1929, **83**, 579; Johnson and Kenyon, J., 1932, 722), and we have found that (+)-αγ-dimethylallyl alcohol on reduction yields optically pure methyl-*n*-propylcarbinol (Pickard and Kenyon, J., 1911, **99**, 65). Even more difficult to explain is the unique form of (—)-αγ-dimethylallyl alcohol produced by hydroxylation of (—)-αγ-dimethylallyl chloride obtained by the action of phosphorus trichloride on the (+)-alcohol in the presence of pyridine. The most remarkable property of this (—)-alcohol is that, although it reacts quantitatively with phthalic anhydride in cold pyridine solution, the resulting hydrogen phthalic ester is optically inactive whereas, under similar conditions, the (+)-alcohol yields a hydrogen phthalic ester with $[\alpha]_{5461}$ + 28·5°.

Many of the observations recorded above can be explained on the assumption that (+)-αγ-dimethylallyl alcohol isomerises very slowly to a *trans*-cyclic isomeride of relatively high lævorotation. At present this simple interpretation cannot be accepted for two reasons. First, on this hypothesis the (+)-alcohol would contain only a small proportion of cyclic isomerides, and therefore some other explanation must be found for the large anomaly in the parachor of the (+)-alcohol; this is not easy to find, since the anomaly is not likely to be due to association—the probable cause of smaller anomalies in the parachors of the lower saturated alcohols (Sugden, *loc. cit.*)—because allyl alcohol possesses a normal parachor. Secondly, this interpretation does not throw any light on the constitution of the novel (—)-alcohol obtained by hydrolysis of (—)-αγ-dimethylallyl chloride. This (—)-alcohol is produced from the (+)-alcohol by the aid of two consecutive reactions, both of which are most likely attended by Walden inversions. It therefore probably has the same configuration as the parent (+)-alcohol. Hence, unless it is assumed that there is more than one lævorotatory isomeric form of the (+)-alcohol, the lævorotatory alcohol produced by mutarotation has the same constitution as the lævorotatory alcohol obtained from (—)-αγ-dimethylallyl chloride. If this be so, then the alcohol produced when the (+)-alcohol undergoes mutarotation cannot be the *trans*-cyclic isomeride, since this would be expected to yield an optically active hydrogen phthalic ester, whereas the lævorotatory alcohol obtained from the chloride yields an optically inactive hydrogen phthalic ester.

It is evident, therefore, that the nature of the isomerism undergone by (+)-αγ-dimethylallyl alcohol will be known with greater certainty when the constitution of the (—)-alcohol obtained by hydrolysis of the chloride has been elucidated.

Experimental.

dl-αγ-Dimethylallyl alcohol was prepared (62% yield) by the interaction of crotonaldehyde (0·9 mol.) and methylmagnesium bromide (1 mol.), and dried over potassium carbonate. The

crude *dl*-alcohol, b. p. 120—125°, had [*P*] 226·7; by distillation through a short column it was separated into three fractions: (i) b. p. 121—121·4°, [*P*] 229·3; (ii) b. p. 121·5—123°; (iii) b. p. 123—124·8°, [*P*] 229·8. No sharp end-points could be obtained when attempts were made to determine the iodine value of $\alpha\gamma$-dimethylallyl alcohol by Wijs's method.

dl-*$\alpha\gamma$-Dimethylallyl Hydrogen Phthalate.*—The *dl*-alcohol (1 mol.), phthalic anhydride (1 mol.), and pyridine (1·1 mols.) were heated on a steam-bath for an hour. The cold homogeneous reaction mixture, when poured into dilute hydrochloric acid and ice, yielded the acid ester as an oil, which solidified (m. p. 88—89°, yield 90%); it separates from methylene chloride in small irregular crystals or from ether–light petroleum in rosettes of small needles, m. p. 90—90·5°.

The Optically Active Dimethylallyl Hydrogen Phthalates.—Brucine (800 g.) was dissolved in a warm solution of the *dl*-hydrogen phthalic ester (468 g.) in a mixture of chloroform (800 c.c.) and acetone (1600 c.c.). The crystals of *l*B,*d*A salt which separated on cooling were obtained optically pure after two recrystallisations from acetone–chloroform. The brucine salt of the racemate tends to separate when acetone alone (Levene and Haller, *loc. cit.*) is used. By working up the mother-liquors, a total yield of 575 g. of the optically pure salt was obtained. *l*-Brucine (+)-$\alpha\gamma$-dimethylallyl phthalate has m. p. 169—169·5° and $[\alpha]_{5461}$ − 15·2 (*c*, 5·6; *l*, in 2) ethyl alcohol; Levene and Haller (*loc. cit.*) record $[\alpha]_{5893}$ − 13·7° at the same concentration. (+)-$\alpha\gamma$-Dimethylallyl hydrogen phthalate, obtained by the decomposition of the brucine salt, has m. p. 82—84°, $[\alpha]_{5893}$ + 38·75° in ether (*c*, 10·0; *l*, 2); Levene and Haller (*loc. cit.*) record $[\alpha]_{5893}$ + 30·8° (*c*, 26·0; *l*, 1) in the same solvent.

The (−)-salt separated as rosettes of fine crystalline rods when the acetone–chloroform filtrates from the less soluble brucine salt were evaporated to small bulk and set aside for several days. After four crystallisations from acetone, it was obtained optically pure, m. p. 157—159°, $[\alpha]_{5461}$ − 8·2° (*c*, 5·0; *l*, 2) in ethyl alcohol. When decomposed it gave (−)-$\alpha\gamma$-dimethylallyl hydrogen phthalate, m. p. 82—84°, $[\alpha]_{5893}$ − 24·1°, $[\alpha]_{5461}$ − 29·4°, $[\alpha]_{4359}$ − 60·7° (*c*, 5·0; *l*, 2) in chloroform solution. A mixture of the (+)- and the (−)-acid phthalic ester softened slightly at 82—84° and melted at 89—90°. The optically active acid esters are more soluble than the *dl*-acid ester; a warm solution of *l* + *dl*-ester ($[\alpha]_{5461}$ − 13° in chloroform) in methylene chloride deposited the *dl*-ester when cooled; *l* + *dl*-ester with $[\alpha]_{5461}$ − 27° was obtained from the filtrate.

Hydrolysis of the Optically Active $\alpha\gamma$-Dimethylallyl Hydrogen Phthalates.—(i) *Hydrolysis of sodium (−)-$\alpha\gamma$-dimethylallyl phthalate by aqueous sodium acetate.* A current of steam was passed through an aqueous solution of the (−)-acid ester (11·7 g., 1 mol.; $[\alpha]_{5461}$ − 13·4°), sodium carbonate (0·5 mol.), and sodium acetate (1 mol.). The $\alpha\gamma$-dimethylallyl alcohol extracted from the steam-distillate was optically inactive both in the homogeneous state and in chloroform solution. Between 20° and 33° its parachor was 233·0.

(ii) *By methyl-alcoholic potassium acetate.* A solution of the (+)-acid ester (47 g.; $[\alpha]_{5461}$ + 30·2° in chloroform solution) and freshly fused potassium acetate (20 g.) in dry methyl alcohol (100 c.c.) was heated under reflux for 70 hours. The cooled mixture was poured into water and extracted with ether; by washing the ethereal layer with sodium carbonate, unchanged (+)-acid ester (11·3 g.) was recovered. On distillation, the dried ethereal extract gave (+)-$\alpha\gamma$-dimethylallyl alcohol, b. p. 119—121° (7·3 g.), $\alpha_{5461}^{18°}$ + 0·27°, $\alpha_{4359}^{18°}$ + 0·64°, (*l*, 0·25); $[\alpha]_{5461}$ − 8·0°, $[\alpha]_{4359}$ − 12·6° (*l*, 2; *c*, 5·25); $[\alpha]_{5461}$ − 8·9°, $[\alpha]_{4359}$ − 13·3° (*l*, 2; *c*, 2·625) in ether. The acid phthalic ester prepared from this alcohol by the method described above had $[\alpha]_{5461}$ + 27·6° (*l*, 2; *c*, 5·0) in chloroform solution.

(iii) *By aqueous sodium hydroxide.* The (+)-$\alpha\gamma$-dimethylallyl alcohol obtained by heating the (+)-acid ester with 5*N*-sodium hydroxide (2·5 mols.) on a steam-bath for 15 mins. had b. p. 119—120°, $\alpha_{5461}^{13°}$ + 1·14° (*l*, 1); $[\alpha]_{5893}$ − 5·8° in ether (*c*, 5; *l*, 2); Levene and Haller (*loc. cit.*) record $[\alpha]_{5893}$ − 6·1° (*c*, 12·1; *l*, 1). It had [*P*] 228·3 between 20° and 25°; a second specimen of the alcohol isolated by similar methods had [*P*] 229·9 between 22° and 45°.

*Reduction of (+)-$\alpha\gamma$-Dimethylallyl Alcohol to (+)-Methyl-*n*-propylcarbinol.*—(+)-$\alpha\gamma$-Dimethylallyl alcohol, from (+)-acid phthalic ester, was reduced in ethereal solution in the presence of platinum oxide to (+)-$\alpha\gamma$-dimethyl-*n*-propyl alcohol (methyl-*n*-propylcarbinol), b. p. 118—119°, $\alpha_{5893}^{17°}$ + 2·71° (*l*, 0·25) [Levene and Haller, *J. Biol. Chem.*, 1929, **83**, 579, carried out this reduction by using colloidal palladium and obtained $\alpha_{5893}^{24°}$ + 7·95° (*l*, 1)]. This was converted into its hydrogen phthalic ester, m. p. 34°, $[\alpha]_{5893}$ + 35·9° (*c*, 5·31; *l*, 2) in chloroform solution. By the resolution of the *dl*-ester with brucine, Pickard and Kenyon (J., 1911, **99**, 63) obtained this (+)-ester with m. p. 34°, $[\alpha]_{5893}$ + 36·9° in chloroform (*c*, 5·0; *l*, 2).

(−)-*$\alpha\gamma$-Dimethylallyl formate*, prepared by heating the (+)-alcohol (5 g.) for ½ hour with the mixed anhydride of formic and acetic acids (9 g.), had b. p. 122—123°, $n_D^{19°}$ 1·4163, $d^{19·6°}$ 0·9139

(Found : C, 62·5; H, 8·6. $C_6H_{10}O_2$ requires C, 63·1; H, 8·8%). The *acetate*, prepared by gently heating the (+)-alcohol with acetic anhydride and pyridine for an hour, had b. p. 136—137°, $n_D^{19°}$ 1·4179, $n_D^{26°}$ 1·4143, $d_{4°}^{25°}$ 0·8931 (Found : C, 65·0; H, 9·5. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%).

(+)-*αγ-Dimethylallyl benzoate*, prepared by the action of benzoyl chloride on a solution of the (+)-alcohol in pyridine, had b. p. 126°/13 mm., $d_{4°}^{25°}$ 1·0108, $n_D^{19°}$ 1·5117 (Found : C, 75·1; H, 7·3. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

(+)-*αγ-Dimethylallyl* o-*nitrobenzoate*, prepared by means of *o*-nitrobenzoyl chloride, had b. p. 124—125°/< 0·1 mm., $d_{4°}^{25°}$ 1·1382, $n_D^{19°}$ 1·5226 (Found : C, 61·0; H, 5·5. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·5%). The m- and the p-*isomeride*, similarly prepared, had respectively b. p. 126—127°/< 0·1 mm., $d_{4°}^{25°}$ 1·1641, $n_D^{19°}$ 1·5327 (Found : N, 6·2. $C_{12}H_{13}O_4N$ requires N, 6·0%), and m. p. 48°, needles from light petroleum (Found : N, 6·1%).

(−)-*Methyl αγ-Dimethylallyl Ether.*—Potassium (3·9 g.) was dissolved in a solution of the (+)-alcohol in ether (50 c.c.), and methyl iodide (14·2 g.) added. After 12 hours, the ethereal solution was washed with water, dried (calcium chloride), and distilled; redistillation of the fraction, b. p. 83—95°, afforded the required *ether*, b. p. 90°, $n_D^{18°}$ 1·4045, $d_{4°}^{15°}$ 0·7729, $\alpha_{5461}^{20°}$ − 14·07°, $\alpha_{4359}^{20°}$ − 23·53° (*l*, 0·25), [*P*] 276·4 (Calc. : 277·2) (Found : C, 71·6; H, 11·8. $C_6H_{12}O$ requires C, 72·0; H, 12·0%).

The n-*butyl* ether, similarly prepared by use of *n*-butyl bromide, had b. p. 149—150°, $d_{4°}^{25·6°}$ 0·7864, $n_D^{18°}$ 1·4192, $\alpha_{5461}^{20°}$ − 7·60°, $\alpha_{4359}^{20°}$ − 12·5° (*l*, 0·25) (Found : C, 76·4; H, 12·3. $C_9H_{18}O$ requires C, 76·1; H, 12·7%), and the *benzyl* ether (benzyl chloride and 4 hours' refluxing) had b. p. 107°/11 mm., $d_{4°}^{25°}$ 0·9698, $n_D^{19°}$ 1·4993, $\alpha_{5461}^{19°}$ − 11·82° (*l*, 0·25) (Found : C, 81·4; H, 9·1. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%).

Conversion of (−)-αγ-Dimethylallyl Alcohol into (−)-Methyl αγ-Dimethylallyl Ether by the Action of Methyl Alcohol and Sulphuric Acid.—A mixture of the (−)-alcohol (5 g.; $\alpha_{5461}^{20°}$ − 0·52°, *l*, 2), methyl alcohol (50 c.c.), and sulphuric acid (2 c.c.) was kept for 24 hours and then poured into ether; the ethereal solution was washed with sodium carbonate, dried with calcium chloride, and distilled, yielding (−)-methyl αγ-dimethylallyl ether, b. p. 90—91°, $n_D^{18°}$ 1·4050, $\alpha_{5461}^{20°}$ − 0·25 (*l*, 0·25), [*P*] 276·9.

Conversion of (−)-αγ-Dimethylallyl Alcohol into dl-n-*Butyl αγ-Dimethylallyl Ether by the Action of* n-*Butyl Alcohol and Sulphuric Acid.*—By the method described in the preceding paragraph, but by using *n*-butyl alcohol, there was obtained *dl*-*n*-butyl αγ-dimethylallyl ether, b. p. 150—151°, $n_D^{15·5°}$ 1·4188, [*P*] 394·3.

Conversion of (−)-αγ-Dimethylallyl Chloride into (−)-αγ-Dimethylallyl Alcohol.—(−)-αγ-Dimethylallyl chloride, prepared from the (+)-alcohol, obtained from the (+)-hydrogen phthalic ester with $[\alpha]_{5461}$ + 30·2° in chloroform, had b. p. 20°/13 mm., $\alpha_{5893}^{16°}$ − 12·46°, $\alpha_{5780}^{16°}$ − 13·02°, $\alpha_{5461}^{16°}$ − 15·14°, $\alpha_{4358}^{16°}$ − 28·8° (*l*, 2) (Found : C, 57·8. Calc. : C, 57·4%). This chloride (10·5 g.) was shaken for 1 hour with a suspension of calcium carbonate (5·3 g.) in water (80 c.c.). The (−)-alcohol, extracted with ether and dried with potassium carbonate, had b. p. 33°/10 mm. and $\alpha_{5893}^{10°}$ − 1·28°, $\alpha_{5780}^{10°}$ − 1·32°, $\alpha_{5461}^{10°}$ − 1·48°, $\alpha_{4358}^{10°}$ − 2·45° (*l*, 2), $n_D^{19°}$ 1·4288 (Found : C, 69·4; H, 11·5. Calc. : C, 69·8; H, 11·6%). It (0·4 g.) was left over-night with a suspension of phthalic anhydride (0·7 g.) in pyridine (1 c.c.), and the resulting solution decomposed with cold dilute hydrochloric acid. The liberated acid phthalic ester (0·8 g.), m. p. 89—90°, was optically inactive in chloroform solution (*c*, 3·5; *l*, 2). A parallel esterification of the (+)-alcohol yielded a hydrogen phthalic ester with $[\alpha]_{5461}$ + 28·5° in chloroform solution.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, *op. cit.*), the apparatus being calibrated by means of benzene.

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128. *A New Method for the Conversion of Acids into Aldehydes.*

By JOHN S. McFADYEN and THOMAS S. STEVENS.

BENZENESULPHONPHENYLHYDRAZIDE (I), when warmed with alkali (Escales, *Ber.*, 1885, **18**, 893), yields benzene, nitrogen, and benzenesulphinic acid, probably *via* the unstable intermediate (II):

$$\text{(I) } NHPh{\cdot}NH{\cdot}SO_2Ph \longrightarrow Ph{\cdot}SO_2K + [Ph{\cdot}N{:}NH] \text{ (II)} \longrightarrow PhH + N_2$$

It is now shown that aldehydes may be obtained in an analogous manner from benzenesulphonacylhydrazides:

$$R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}SO_2Ph \longrightarrow Ph{\cdot}SO_2K + [R{\cdot}CO{\cdot}N{:}NH] \longrightarrow R{\cdot}CHO + N_2$$

and the generality of the method has been investigated.

The percentage yields of aldehydes obtained from the corresponding benzenesulphonacylhydrazides are recorded in Table I. Those of the aromatic aldehydes are often very good, but the method fails entirely in the aliphatic series. The contrasting behaviour of the benzenesulphon-nitrobenzoylhydrazides recalls the experience of Curtius and Melsbach (*J. pr. Chem.*, 1910, **81**, 524), who found that *m*-nitrobenzhydrazide in weakly alkaline solution yielded *m*-nitrobenz-*m'*-nitrobenzylidenehydrazide, whereas the *p*-isomeride underwent no analogous reaction.

TABLE I.

{A	Benzoic	73	F	*p*-Methoxybenzoic	77	K	† Cinnamic	0
{B	* Benzoic	74	G	3 : 4-Methylenedioxybenzoic	87	L	Acetic	0
C	* *p*-Chlorobenzoic	77	H	*m*-Nitrobenzoic	42	M	*iso*Butyric	0
{D	*o*-Hydroxybenzoic	55	J	*p*-Nitrobenzoic	0	N	Diphenylacetic	0
{E	* *o*-Hydroxybenzoic	42						

* The 2 : 5-dichlorobenzenesulphonacylhydrazide was used.

† The action of benzenesulphonyl chloride on cinnamoylhydrazine yielded a *compound*, white rhombs from alcohol, m. p. 169—171° (decomp.) (Found: N, 9·7, 9·8. $C_{15}H_{14}O_3N_2S$ requires N, 9·3%), from which no cinnamaldehyde could be obtained.

The required benzenesulphonacylhydrazides may be prepared according to the scheme:

$$R{\cdot}CO_2H \longrightarrow R{\cdot}CO_2Et \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}NH_2(+\ Ph{\cdot}SO_2Cl) \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}SO_2Ph \quad \text{(X)}$$

$$R{\cdot}CO_2H \longrightarrow R{\cdot}COCl(+Ph{\cdot}SO_2{\cdot}NH{\cdot}NH_2) \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}SO_2Ph \quad \text{(Y)}$$

but the action of the acid chloride on benzenesulphonhydrazide in the benzoyl and anisoyl series led to very ready diacylation, and the route (X) was therefore in general preferred to the route (Y). The benzenesulphonacylhydrazides are represented here as having the symmetrical structure, with no free amino-group, since *benzenesulphonbenzoylhydrazide* did not react with benzaldehyde in boiling alcohol.

This type of reaction has also been applied successfully to the replacement, by hydrogen, of a reactive halogen atom in the benzene ring. Thus 2 : 4-dinitrochlorobenzene gave *m*-dinitrobenzene, and picryl chloride yielded *s*.-trinitrobenzene, which may be simply and rapidly prepared by the series of reactions:

$$C_6H_2(NO_2)_3{\cdot}OH \longrightarrow C_6H_2(NO_2)_3Cl \longrightarrow C_6H_2(NO_2)_3{\cdot}NH{\cdot}NH{\cdot}SO_2Ph \longrightarrow C_6H_3(NO_2)_3$$

EXPERIMENTAL.

The known acid hydrazides were obtained in good yield by published methods. *Piperonoylhydrazine* was prepared by refluxing methyl piperonylate (5 g.), 50% hydrazine hydrate (5·6 c.c.), and alcohol (6 c.c.) for 2 hours. The needles (4 g.; m. p. 170—171°) which separated over-night were collected, and the filtrate and washings (ice-cold alcohol) on concentration and further refluxing yielded 0·6 g. more. The hydrazide crystallised from alcohol in small colourless needles, m. p. 171—172° (Found: N, 15·7. $C_8H_8O_3N_2$ requires N, 15·6%).

The benzenesulphonacylhydrazides (all colourless) were prepared as described for the benzoyl series, usually by method (X) with an average yield of 90%; the descriptions and analytical data are in Table II.

Benzenesulphonbenzoylhydrazide.—(X) Benzenesulphonyl chloride (3·8 c.c.) was added slowly to a stirred, cooled solution of benzhydrazide (4 g.) in pyridine (25 c.c.). After 2 hours the solution was poured into a mixture of ice and hydrochloric acid, and the pale yellow precipitate filtered off, washed with dilute hydrochloric acid and water, and recrystallised from alcohol (80 c.c.). Yield, 7 g. of colourless prismatic needles, m. p. 192—194° (decomp.) (Found: N, 10·4. $C_{13}H_{12}O_3N_2S$ requires N, 10·15%).

(Y) Benzoyl chloride (26·8 c.c.) was added slowly to a stirred, cooled solution of benzenesulphonhydrazide (40 g.) in pyridine (100 c.c.). The solution was poured with stirring into a mixture of ice and hydrochloric acid, and the white precipitate was washed with dilute hydrochloric acid and water. Yield of crude material, 55 g. Recrystallisation from alcohol gave a first crop (2 hours) of colourless prismatic needles (30 g.), m. p. 191—193° (decomp.), not depressed on admixture with the product from method (X) above. After 2 days the mother-liquor deposited a further crop of the above product, together with colourless silky needles. By repeated warming, filtration, and recrystallisation the more easily soluble fine needles were obtained as an apparently homogeneous product, m. p. 192—194° (decomp.), depressed on admixture with benzenesulphonbenzoylhydrazide, but not with *benzenesulphondibenzoylhydrazide.*

Benzenesulphondibenzoylhydrazide.—Benzenesulphonbenzoylhydrazide (1·1 g.) and benzoyl chloride (0·72 g.) were kept in pyridine (10 c.c.) at 40° for 4 hours. The mixture was poured into water and ligroin, and vigorously shaken. The solid product was filtered off and recrystallised from alcohol, giving silky needles, m. p. 198—200° (decomp.) (Found: N, 7·4. $C_{20}H_{16}O_4N_2S$ requires N, 7·4%).

TABLE II.

Benzenesulphonacylhydrazides.

Acyl.	Solvent.	Description.	M. p.	% N found.	% N required.	Formula.
* Benzoyl	EtOH	Prismatic needles	186—188° ‡	8·4	8·1	$C_{13}H_{10}O_3N_2Cl_2S$
* *p*-Chlorobenzoyl	EtOH	Prisms	235—237 ‡	7·5	7·4	$C_{13}H_9O_3N_2Cl_3S$
o-Hydroxybenzoyl	EtOH	Silky needles	161—162	9·8	9·6	$C_{13}H_{12}O_4N_2S$
* *o*-Hydroxybenzoyl	EtOH	Needles	229—230 ‡	7·8	7·8	$C_{13}H_{10}O_4N_2Cl_2S$
p-Methoxybenzoyl	EtOH	Prisms	187—189 ‡	9·3	9·2	$C_{14}H_{14}O_4N_2S$
3 : 4-Methylenedioxybenzoyl	EtOH	Prisms	166—168	8·8	8·8	$C_{14}H_{12}O_5N_2S$
m-Nitrobenzoyl	HOAc	Fibrous needles	222—223 ‡	12·9	13·1	$C_{13}H_{11}O_5N_3S$
† *p*-Nitrobenzoyl	EtOH	Silky needles	197—199 ‡	13·1	13·1	$C_{13}H_{11}O_5N_3S$
Acetyl (Curtius and Lorenzen, *J. pr. Chem.*, 1898, **58**, 173)						
*iso*Butyryl	EtOH	Rhombs	156—158	11·7	11·6	$C_{10}H_{14}O_3N_2S$
Diphenylacetyl	EtOH	Plates	191—193	7·8	7·7	$C_{20}H_{18}O_3N_2S$

* 2 : 5-Dichlorobenzenesulphonacylhydrazides.
† Prepared by route (Y); reaction completed at 50°.
‡ Melting with decomposition.

Decomposition of Benzenesulphonacylhydrazides.—This was brought about by alkaline carbonates; sodium borate or acetate, or organic bases were ineffective. When the aldehyde was steam-volatile and insoluble in alkali, the decomposition, if taking place readily, could conveniently be brought about by steam-distillation from aqueous sodium carbonate. Otherwise ethylene glycol was used as solvent on account of its high b. p., ability to dissolve alkaline carbonates, and miscibility with water, which facilitated isolation of the product. Experiments with other solvents, such as pyridine, quinoline and *cyclo*hexanol, were less encouraging. Benzenesulphinic acid was produced in quantity and identified as 2 : 4-dinitrodiphenylsulphone (mixed m. p.).

Table III contains the results of a few typical experiments. In these, benzenesulphonbenzoylhydrazide was dissolved in glycol heated in an oil-bath at the specified temperature, and anhydrous alkali added in one portion, causing brisk effervescence; after the specified time the reaction was stopped by the addition of hot water. The washed and dried ethereal extract of the resulting solution was evaporated, and the residual aldehyde precipitated and weighed

as the *dinitrophenylhydrazone*. On the preparative scale the percentage yield of redistilled aldehyde was slightly smaller than that of the dinitrophenylhydrazone in the corresponding small-scale experiment.

TABLE III.

Experiment No.	1.	2.	3.	4.	5.	6.	7. †	8. †
Temperature	80→90°	130°	160°	160°	165°	140→190°	110°	‡
Time (secs.)	4000	1000	75	40	60	1000	500	‡
Equivs. alkali	6	4 *	5	2	1 *	4 *	4	6
Yield %	30	40	73	60	46	10	74	65

* Potassium carbonate; in all other cases sodium carbonate.

† Initial material 2 : 5-dichlorobenzenesulphonbenzoylhydrazide.

‡ Carried out by steam-distillation from aqneous sodium carbonate.

Except in experiment 6, the given time of heating is as short as is consistent with complete decomposition.

General Observations.—(a) The quantity of solvent (5 to 20 parts) had little effect on the yield. (b) Sodium carbonate as alkali gave slightly better results than the potassium salt. (c) The optimum temperature was about 160° (1, 2, 3); prolonged heating at a high temperature gave poor results (6). (d) Considerable excess of alkali was necessary (3, 4, 5). (e) The dichlorobenzenesulphonhydrazide decomposed at a lower temperature, giving a very similar yield (7, 8).

The other benzenesulphonacylhydrazides were treated in a similar manner, except that the alkali-soluble salicylaldehyde was steam-distilled from the acidified reaction mixture, and estimated as the dinitrophenylhydrazone. The yields given in Table I were obtained under the following conditions:

Case	C.	D.	E.	F.	G.	H.
Temperature	80→110°	155°	160°	150°	155°	155°
Time (secs.)	900	180	40	120	150	75
Equivs. Na_2CO_3	5	5	4	6	6	6

In case J the only product isolated was a crude, buff-coloured amorphous solid, softening at about 220°, but not completely melted at 290°. The initial materials in cases L and M were heated with sodium carbonate in a variety of high-boiling solvents, the vapours being led by a gentle air stream directly into the dinitrophenylhydrazine reagent, but no aldehyde was detected.

Benzenesulphon-2′ : 4′-dinitrophenylhydrazide.—2 : 4-Dinitrophenylhydrazine (4 g.) was suspended in pyridine (25 c.c.) at 50°, and vigorously stirred during the addition (15 mins.) of benzenesulphonyl chloride (2·8 c.c.). After 2 hours' stirring at room temperature, the product was poured into dilute caustic soda solution, and filtered from unchanged dinitrophenylhydrazine. The filtrate, on acidification, gave a brownish-yellow precipitate, which on recrystallisation from alcohol (animal charcoal) gave a mixture of lemon-yellow laminæ, m. p. 196—198° (decomp.) (Found: N, 16·4. $C_{12}H_{10}O_6N_4S$ requires 16·6%), and fine yellow needles, m. p. 196—198° (decomp.) (Found: N, 16·5%), showing no depression on admixture with one another, but each depressed by dinitrophenylhydrazine. In contact with alcohol, the needles gradually changed to the laminæ at room temperature.

Decomposition. Sodium carbonate (1 g.) was added to *benzenesulphon-2′ : 4′-dinitrophenylhydrazide* (1 g.) in ethylene glycol (10 c.c.) at 150°. After 3 minutes, hot water was added, and the mixture cooled. The chocolate-brown precipitate (0·34 g.; 70%), m. p. 81—83°, was recrystallised from alcohol (animal charcoal), giving pale yellow plates, m. p. 90°, not depressed on admixture with *m*-dinitrobenzene.

Benzenesulphon-2′ : 4′ : 6′-trinitrophenylhydrazide.—Hot alcoholic solutions of picryl chloride (15 g. in 120 c.c.) and benzenesulphonhydrazide (10 g. in 75 c.c.) were mixed and refluxed for a few minutes with shaking. The solid which rapidly separated was filtered off after cooling and washed with hot alcohol. It crystallised from alcohol (1000 parts) in lemon-yellow fibrous needles, m. p. 210—220° (decomp.) (Found: N, 18·3. $C_{12}H_9O_8N_5S$ requires N, 18·3%).

Decomposition. A mixture of *benzenesulphon-2′ : 4′ : 6′-trinitrophenylhydrazide* (9 g.), borax (5 g.), and water (50 c.c.) was heated carefully until the first effervescence was over, and then boiled for 40 minutes. After thorough cooling, the dark brown, amorphous solid (crude trinitrobenzene) was collected. This was recrystallised twice from alcohol (animal charcoal), giving 3 g. of pale yellow plates, m. p. 121—122°, not depressed on admixture with pure 1 : 3 : 5-trinitrobenzene.

The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of them (J. S. McF.), and to Mr. J. M. L. Cameron for carrying out the (micro) nitrogen analyses.

THE UNIVERSITY, GLASGOW. [*Received, March 4th, 1936.*]

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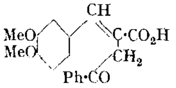
129. *Syntheses of 1-Phenylnaphthalenes.*

By WILLIAM N. HOWELL and ALEXANDER ROBERTSON.

THE work described in this paper was undertaken as a continuation of a synthetical contribution to the structure of podophyllotoxin and its degradation products (J., 1933, 83), but when it became known to us that a similar investigation, having the same objective, had reached a more advanced stage in Dr. R. D. Haworth's laboratory (private communication) we decided to abandon our project (compare Haworth and co-workers, J., 1935, 1576). When our experiments were initiated in 1934 it appeared from the literature that little attention had been devoted to the synthesis of 1-phenylnaphthalenes. 1-Phenyl- and 1-*p*-tolyl-naphthalene had been obtained by dehydrogenation of the corresponding dihydro-derivatives prepared by the interaction of α-tetralone with phenyl- and tolylmagnesium bromide respectively (Weiss and Woidich, *Monatsh.*, 1925, **46**, 453; Braun and Anton, *Ber.*, 1934, **67**, 1051), but for the preparation of polymethoxy-derivatives having a skeleton of the podophyllotoxin type this method has obvious limitations. Nevertheless it was decided to utilise this procedure for the preparation of reference compounds which would serve as a check on the products obtained by other methods. As an example, decarboxylation of the acid (III, R = CO_2H), formed by cyclisation of the *keto-acid* (I) or its *lactone* (II), gives rise to the *naphthalene* (III, R = H), identical with the product obtained by the dehydrogenation of the *dihydro*-derivative (IV). The last compound was prepared by the interaction of phenylmagnesium bromide and the appropriate tetralone.



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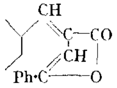

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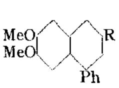

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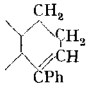


(IV.)

EXPERIMENTAL.

4'-Methoxy-1-phenylnaphthalene.—α-Tetralone (26 g.) in ether (100 c.c.) was gradually added to a solution of *p*-anisylmagnesium bromide (from 7·4 g. of metal and 57 g. of *p*-bromoanisole in 75 c.c. of ether) and 12 hours later the mixture was refluxed for 2 hours. The product was hydrolysed in the usual manner, the ether and unchanged tetralone removed with steam, and *4'-methoxy-1-phenyl-3 : 4-dihydronaphthalene* (22 g.), b. p. 198—200°/12 mm., isolated from the residual product by fractional distillation in a vacuum, forming colourless diamond-shaped plates, m. p. 76°, from alcohol, easily soluble in the usual organic solvents except alcohol (Found: C, 86·4; H, 6·9; OMe, 12·6. $C_{16}H_{13}$·OMe requires C, 86·4; H, 6·8; OMe, 13·1%).

Dehydrogenation of the dihydro-compound (2 g.) with powdered selenium (2 g.) at 280—300° for 24 hours gave a product (1·5 g.) from which *4'-methoxy-1-phenylnaphthalene* was isolated by repeated crystallisation from 70% alcohol, being finally obtained in colourless needles, m. p. 116·5°, easily soluble in acetic acid or benzene (Found: C, 87·2; H, 6·0. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%). Nitration of this substance (0·8 g.) in acetic acid (5 c.c.) with nitric acid (1·2 c.c., *d* 1·4) at room temperature in the course of 4 hours gave a *mononitro*-derivative, which separated from alcohol in long yellow needles (0·6 g.), m. p. 129° (Found in material dried at 80° in a high vacuum: N, 5·1. $C_{17}H_{13}O_3N$ requires N, 5·0%).

6 : 7-Dihydroxy-1-phenylnaphthalene.—*6 : 7-Dimethoxy-1-phenyl-3 : 4-dihydronaphthalene* was prepared from 6 : 7-dimethoxy-α-tetralone (17 g.) and phenylmagnesium bromide (from 26·4 g. of bromobenzene) in ether (300 c.c.) and purified by distillation in a vacuum and then by crystallisation from 95% alcohol, forming colourless hexagonal plates (16·8 g.), b. p. 215—217°/14 mm., m. p. 88·5°, readily soluble in benzene or light petroleum and moderately easily soluble in

acetic acid [Found: C, 81·3; H, 6·8; OMe, 23·0. $C_{16}H_{12}(OMe)_2$ requires C, 81·2; H, 6·8; OMe, 23·3%]. Dehydrogenation of this compound (2 g.) with selenium (2 g.) at 280—300° for 24 hours gave an ether-soluble product (1·4 g.), from which *6 : 7-dimethoxy-1-phenylnaphthalene* was isolated by repeated crystallisation, from alcohol, forming colourless needles, m. p. 110°, having solubilities almost identical with those of the dihydro-derivative (Found: C, 81·8; H, 6·1. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

Demethylation of the dimethyl ether (1·75 g.) by heating with a mixture of hydriodic acid (50 c.c., *d* 1·7) and acetic anhydride (30 c.c.) at 140—145° for 50 minutes gave rise to the *dihydroxy*-compound (1·4 g.), which separated from warm water and then light petroleum (b. p. 60—80°) in colourless needles, m. p. 167—168°, easily soluble in benzene or alcohol (Found: C, 81·7; H, 5·2. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%). This compound gives a royal-blue ferric chloride reaction and a deep red coloration with concentrated sulphuric acid.

7-Methoxy-1-phenylnaphthalene.—Prepared from 7-methoxy-α-tetralone by the Grignard reaction, *7-methoxy-1-phenyl-3 : 4-dihydronaphthalene* was purified by distillation in a vacuum and then by crystallisation from 95% alcohol, forming elongated hexagonal plates, m. p. 42·5—43·5°, easily soluble in benzene, light petroleum, or chloroform (Found: C, 86·7; H, 6·9; OMe, 13·1. $C_{16}H_{13}$·OMe requires C, 86·4; H, 6·8; OMe, 13·1%). Dehydrogenation of this substance with selenium at 280—300° gave a product, b. p. 210—222°/19 mm., from which *7-methoxy-1-phenylnaphthalene* was isolated by fractional distillation over sodium in a vacuum, being finally obtained as a colourless oil, b. p. 214—215°/19 mm., with a faint blue fluorescence, which solidified in the course of 6 months; m. p. 48—50° (Found: C, 87·3; H, 6·2. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%).

4'-Methoxy-1-phenyl-2-methylnaphthalene.—Prepared by the Grignard method, the 3 : 4-*dihydro*-derivative was contaminated with *pp'*-dianisyl, from which it was separated by fractional crystallisation from light petroleum (b. p. 60—80°), forming diamond-shaped plates, m. p. 91—92° (Found: C, 86·0; H, 7·4; OMe, 12·5. $C_{17}H_{15}$·OMe requires C, 86·4; H, 7·2; OMe, 12·4%). On dehydrogenation this compound gave the *naphthalene*, which crystallised from 50% alcohol in hexagonal plates and from dilute acetic acid in needles, m. p. 108° (Found: C, 87·3; H, 6·6. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%).

β-Benzoyl-α-veratrylidenepropionic Acid (I).—Condensation of sodium β-benzoylpropionate (16·2 g.) and veratraldehyde (25 g.) by means of acetic anhydride (50 c.c.) at 100° during 12 hours (method of Borsche, *Ber.*, 1914, **47**, 1108) gave rise to the *γ-lactone* of the acid (15·5 g.), which crystallised from warm (not boiling) methyl alcohol in golden-yellow plates, m. p. 131°, easily soluble in benzene or chloroform and sparingly soluble in cold acetic acid (Found: C, 74·1; H, 5·3. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). On being boiled with methyl alcohol for 5 minutes, the lactone was converted into the *methyl* ester of the acid, which separated from the cooled solution in colourless needles, m. p. 96° after recrystallisation (Found: C, 70·5; H, 5·9. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

Treatment of the lactone (5 g.) with cold alcoholic sodium methoxide (from 0·35 g. of sodium and 50 c.c. of methyl alcohol) gave rise to a mixture of the ester (2·5 g.) and the *acid*. The latter substance formed colourless plates (1·5 g.), m. p. 168°, from dilute acetic acid, easily soluble in chloroform or methyl alcohol (Found: C, 69·8; H, 5·8. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%).

6 : 7-Dimethoxy-1-phenylnaphthalene-3-carboxylic acid (III, R = CO_2H) separated from a solution of the foregoing lactone (1·7 g.) in chloroform (20 c.c.) containing iodine (1·7 g.) in the course of 5 days at room temperature. Crystallised from dilute methyl alcohol, the compound formed colourless stout rods (0·7 g.), m. p. 265° (Found: C, 74·4; H, 5·4. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). A further quantity (0·6 g.) was obtained from the chloroform liquor.

On being heated with methyl alcohol saturated with hydrogen chloride for 4 hours β-benzoyl-α-veratrylidenepropionic acid or its methyl ester gave rise to the methyl ester of (III, R = CO_2H), forming clusters of colourless needles, m. p. 124°, from methyl alcohol, which on hydrolysis with boiling 6% aqueous-alcoholic potassium hydroxide for 2 hours yielded the naphthalene-3-carboxylic acid, m. p. and mixed m. p. 265°, after purification.

Decarboxylation of this acid (0·23 g.) by boiling with quinoline (3 c.c.) in the presence of copper bronze (0·2 g.) for 2 hours furnished 6 : 7-dimethoxynaphthalene (III, R = H), forming long needles, m. p. 110°, from 50% aqueous alcohol, identical with an authentic specimen prepared from 6 : 7-dimethoxy-α-tetralone.

β-p-Anisoyl-α-benzylidenepropionic Acid.—Condensation of sodium β-*p*-anisoylpropionate (35 g.) and benzaldehyde (32 g.) with acetic anhydride (64 c.c.) at 100° for 12 hours yielded the *γ-lactone* of the acid, which separated from benzene in greenish-yellow needles (25 g.), m. p. 174° (Found: C, 77·6; H, 4·9. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%). The lactone (2 g.) gradually

dissolved in methyl alcohol (20 c.c.) containing sodium methoxide (from 0·17 g. of sodium). Addition of water to the solution precipitated the *methyl* ester, which formed colourless needles, m. p. 74—75°, from methyl alcohol (Found: C, 73·4; H, 5·8. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%).

The *acid* was isolated from the concentrated alkaline liquor and on crystallisation from benzene formed colourless needles, m. p. 170°, containing solvent of crystallisation (Found: C, 75·0; H, 5·7. $C_{18}H_{16}O_4,0·5C_6H_6$ requires C, 75·2; H, 5·7%. Found in material dried at 80° in a high vacuum: C, 73·4; H, 5·3. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%).

Attempts to effect cyclisation of this acid (or its ester) with alcoholic hydrogen chloride or sulphuric acid were unsuccessful. In the case of the lactone negative results were also obtained with iodine and chloroform.

ω-*Chloro*-3 : 4 : 5-*trimethoxyacetophenone* (7 g.) was prepared by treating ω-diazo-3 : 4 : 5-trimethoxyacetophenone (Robinson and co-workers, J., 1933, 374) (8 g.) with excess of hydrogen chloride in ether (500 c.c.) at 0°. Crystallised from ether–light petroleum (b. p. 60—80°), the compound formed rhombic prisms, m. p. 86—87° (Found: C, 54·5; H, 5·5. $C_{11}H_{13}O_4Cl$ requires C, 54·0; H, 5·3). A solution of this substance (1 g.) in alcohol (20 c.c.) containing potassium acetate (1 g.) and a crystal of sodium iodide was refluxed for 1 hour, cooled, and diluted with water. Crystallisation of the resulting solid (1 g.) from alcohol gave ω-*acetoxy*-3 : 4 : 5-*trimethoxyacetophenone* in colourless needles, m. p. 85—86° (Found: C, 58·2; H, 6·1. $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0%).

β-(3 : 4 : 5-*Trimethoxybenzoyl*)*propionic Acid*.—Interaction between the foregoing chloro-compound (12·5 g.) and ethyl sodiomalonate (from 7·5 g. of ester and 1·15 g. of sodium) in boiling benzene was complete in 2 hours. The product was hydrolysed with boiling 30% alcohol (50 c.c.) containing potassium hydroxide (10 g.) for 3 hours; the resulting *malonic acid* (6 g.) crystallised from ethyl acetate–light petroleum (b. p. 60—80°) in plates, m. p. 167—168° (decomp.) (Found: C, 54·2; H, 5·3. $C_{14}H_{16}O_8$ requires C, 53·8; H, 5·1%). On being kept at 160° for ½ hour, this compound was converted into the propionic acid, separating from water in needles which melted at 116° and then on solidification changed into the form, m. p. 122° (Found: C, 58·3; H, 6·1. Calc. for $C_{13}H_{16}O_6$: C, 58·2; H, 6·0%) (compare Haworth and co-workers, *loc. cit.*, who give m. p. 121—122°).

Condensation of the sodium salt of this acid (2·6 g.) with veratraldehyde (3·3 g.) in the usual manner furnished the γ-*lactone* of β-(3 : 4 : 5-trimethoxybenzoyl)-α-veratrylidenepropionic acid, forming golden needles, m. p. 172—173°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 66·3; H, 5·7. $C_{22}H_{22}O_7$ requires C, 66·3; H, 5·6%).

The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant awarded to one of them (W. N. H.).

UNIVERSITY OF LIVERPOOL. [*Received, April 14th,* 1936.

130. *Glycerol Ethers of Resacetophenone.*

By D. R. NADKARNI and T. S. WHEELER.

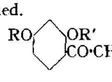
MOTWANI and WHEELER (J., 1935, 1098) studied the preparation of β-hydroxyethyl ethers of resacetophenone with a view to synthesising substances containing coumaran and γ-pyrone nuclei. We have examined the reactions between resacetophenone and glycerol α-monochlorohydrin and epichlorohydrin with a view to preparing glycerol ethers of resacetophenone, to be eventually employed in the synthesis of flavone derivatives of the type prepared by Motwani and Wheeler (*loc. cit.*). The interactions of glycerol, glycide, and glycerol α-monochlorohydrin with phenols have been studied previously by a number of workers; a summary of their results has been given by Marle (J., 1912, **101**, 305).

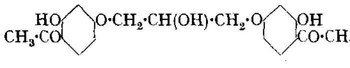
The condensation of glycerol α-monochlorohydrin with resacetophenone in the presence of dilute potassium hydroxide solution gave 2-*hydroxy*-4-(βγ-*dihydroxypropoxy*)*acetophenone* [I; R = $CH_2(OH)·CH(OH)·CH_2$, R′ = H] (70% yield) and *glycerol* αγ-*bis*-(3-*hydroxy*-4-*acetylphenyl*) *ether* (II) (20% yield); higher concentrations of the alkali gave larger yields of (II). The structure of (II) was confirmed by its preparation from epichlorohydrin,

resacetophenone, and sodium ethoxide by Boyd and Marle's method (J., 1908, **93**, 838) for glycerol αγ-diphenyl ether.

Epichlorohydrin, when condensed with resacetophenone in aqueous sodium hydroxide (Boyd and Marle, loc. cit.), gave 2-hydroxy-4-βγ-epoxypropoxyacetophenone (I; R = $O<{CH_2 \atop CH{\cdot}CH_2}$, R′ = H) and presumably 2 : 4-*bis*-(βγ-*epoxypropoxy*)*acetophenone*. The latter substance could not be purified.

2-*Hydroxy*-4-γ-*chloro*-β-*hydroxypropoxyacetophenone* [I; R = $CH_2Cl{\cdot}CH(OH){\cdot}CH_2$, R′ = H] was obtained from epichlorohydrin and resacetophenone with 10% sodium hydroxide solution (1/80 mol.) as a catalyst (Boyd and Marle, J., 1910, **97**, 1789). With higher proportions of the alkali the monoglycide ether (I; R = $O<{CH_2 \atop CH{\cdot}CH_2}$, R′ = H) also separated.

(I.) 

 (II.)

EXPERIMENTAL.

2-*Hydroxy*-4-(βγ-*dihydroxypropoxy*)*acetophenone*.—A solution of potassium hydroxide (56 g.) in water (200 g.) was added to resacetophenone (76 g.) suspended in ice-cold water (75 c.c.), and the mixture heated with glycerol α-chlorohydrin (110·5 g.) at 100° for 3 hours. The oil (II, see below) which separated was removed, and the mother-liquor kept in the refrigerator for 48 hours. The resulting precipitate (yield, 70%) crystallised from aqueous alcohol in thin plates, m. p. 88°. It was soluble in water and gave a violet coloration with alcoholic ferric chloride (Found : C, 58·2; H, 6·2. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%).

The *hydrazone*, obtained by warming an alcoholic solution with 50% hydrazine hydrate, crystallised from aqueous alcohol in pale yellow needles, m. p. 98° (Found : N, 11·5. $C_{11}H_{16}O_4N_2$ requires N, 11·7%). The *azine*, obtained by treatment of the ketone with hydrazine hydrate in glacial acetic acid, crystallised from alcohol in yellow needles, m. p. 292—294° (Found : N, 6·6. $C_{22}H_{28}O_8N_2$ requires N, 6·3%). The *phenylhydrazone*, crystallised from rectified spirit, had m. p. 119—120° (Found : N, 9·0. $C_{17}H_{20}O_4N_2$ requires N, 8·9%).

Glycerol αγ-*Bis*-(3-*hydroxy*-4-*acetylphenyl*) *Ether* (II).—The separated oil (II above; yield, 20%) solidified in the refrigerator and then crystallised from acetone in colourless needles, m. p. 161°. It was soluble in alkali and gave a violet coloration with alcoholic ferric chloride. It was also obtained when epichlorohydrin (45 g.) was heated with sodium (12 g.), alcohol (300 c.c.), and resacetophenone (152 g.) at 100° under reflux for 4 hours, and the mixture diluted with water (Found : C, 63·4; H, 5·6. $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·6%).

The *hydrazone*, crystallised from alcohol, had m. p. 184° (Found : N, 14·2. $C_{19}H_{24}O_5N_4$ requires N, 14·4%). The *azine*, insoluble in all solvents, was purified by extraction with boiling acetic acid; m. p. above 300° (Found : N, 7·9. $C_{38}H_{40}O_{10}N_4$ requires N, 7·9%). The *phenylhydrazone* crystallised from alcohol in needles, m. p. 206° (Found : N, 10·2. $C_{31}H_{32}O_5N_4$ requires N, 10·4%).

2-*Hydroxy*-4-βγ-*epoxypropoxyacetophenone*.—An amorphous solid separated when a mixture of epichlorohydrin (23 g.), resacetophenone (38 g.), sodium hydroxide (12 g.), and water (250 c.c.) was kept at room temperature for a week. It was sparingly soluble in boiling glacial acetic acid, but did not separate except on dilution; it then formed a sticky mass. On addition of hydrazine hydrate to the boiling acetic acid solution an azine (?) insoluble in all solvents separated; for purification, it was extracted with boiling glacial acetic acid; m. p. above 300° [Found : C, 61·1; H, 6·4; N, 5·7. $C_{28}H_{32}O_8N_2$ (azine of I; R = R′ = $O<{CH_2 \atop CH{\cdot}CH_2}$) requires C, 64·1; H, 6·1; N, 5·3%]. A similar compound was also obtained by heating a mixture of epichlorohydrin (37 g.), resacetophenone (30·4 g.), potassium hydroxide (20 g.), and water (20 c.c.) at 120° for 3 hours (Found for the insoluble azine : C, 60·1; H, 6·2; N, 5·1%).

When the mother-liquor obtained after the removal of the presumed diglycide ether in the above condensation at room temperature was acidified with dilute hydrochloric acid, a sticky mass separated; repeatedly crystallised from acetic acid and finally from rectified spirit, it formed colourless needles, m. p. 78°. It was soluble in alkali and gave a violet coloration with alcoholic ferric chloride (Found : C, 63·4; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

The *acetyl* derivative (I; $R = O{<}^{CH_2}_{CH \cdot CH_2}$, $R' = CO{\cdot}CH_3$), obtained by boiling the monoglycide ether with glacial acetic acid, crystallised from acetic acid as a reddish-brown powder, m. p. 198—200° (Found : C, 62·2; H, 5·8. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6%).

The monoglycide ether did not give [I; $R = CH_2(OH){\cdot}CH(OH){\cdot}CH_2$, $R' = H$] when heated with water in a sealed tube at 180° for 24 hours, though Lindemann (*Ber.*, 1891, **24**, 2149) and Marle (*loc. cit.*) have observed that phenyl glycide ethers react with water to produce glycerol aryl ethers under these conditions.

2-*Hydroxy*-4-γ-*chloro*-β-*hydroxypropoxyacetophenone*.—A mixture of epichlorohydrin (92·5 g.), resacetophenone (152 g.), sodium hydroxide (0·5 g.), and water (5 c.c.) was kept at room temperature for 6 weeks. It was then extracted with ether, and the excess of epichlorohydrin removed from the extract by distillation under reduced pressure. The oily residue solidified in the refrigerator after a week and then crystallised from rectified spirit in needles, m. p. 68° after softening at 58°. It was soluble in alkali and gave a violet coloration with alcoholic ferric chloride. The substance liquefied when kept over sulphuric acid and resolidified when exposed to air [Found: Cl, 13·6; loss after drying at 120°/2 mm. (a liquid resulted), 6·8. $C_{11}H_{13}O_4Cl,H_2O$ requires Cl, 13·5; H_2O, 6·9%. Found after drying: Cl, 14·9. $C_{11}H_{13}O_4Cl$ requires Cl, 14·5%].

When dissolved in aqueous sodium hydroxide and then acidified with acetic acid, this ether gave the monoglycide ether (I; $R = O{<}^{CH_2}_{CH \cdot CH_2}$, $R' = H$), which on heating with concentrated hydrochloric acid at 100° for 2 hours reproduced the chlorohydrin ether.

All the analyses are micro-analyses carried out by Dr. Schoeller of Berlin or Dr. J. N. Ray of Lahore, to whom our thanks are due. We are grateful to the Dabholker Research Scholarship Trust for a scholarship, and to the University of Bombay for a grant, awarded to one of us (D. R. N.).

ROYAL INSTITUTE OF SCIENCE, BOMBAY. [*Received, March 9th*, 1930.]

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131. *The Constitution of Oroxylin-A, a Yellow Colouring Matter from the Root-bark of* Oroxylum indicum, *Vent.*

By R. C. SHAH, C. R. MEHTA, and T. S. WHEELER.

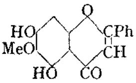
OROXYLIN was isolated by Naylor and Chaplin (" Year Book of Pharmacy," 1890) from the root bark of *Oroxylum indicum*, Vent, an Indian medicinal plant (natural order *Bignoniaceæ*). Naylor and Dyer (J., 1901, **79**, 954) assigned to it the formula $C_{19}H_{14}O_6$ (cf. Warner, *Pharm. J.*, 1898, **7**, 390) and inferred the presence of three hydroxyl groups from the preparation of an acetyl derivative which, from the amount of oroxylin it gave on hydrolysis, was assumed to be a triacetate. Hydrolysis with concentrated alkali yielded phthalic and benzoic acids, and a neutral product which gave the pinewood and hydrochloric acid test for phloroglucinol. Dilute alkali produced benzaldehyde, and potassium permanganate, phthalic acid. Methoxy-, carbonyl, and carboxyl groups appeared to be absent.

The root bark used in the present investigation was purchased from Ahmednagar Ayurvedashram, or collected from the Songadh forests in Gujarat, and was identified by Dr. K. S. Mhaskar of the Haffkine Institute, Bombay, to whom our thanks are due. We isolated oroxylin by a method similar to that of Naylor and Dyer (0·2% yield) and also by a new method (0·86% yield). The properties of our product as regards appearance, m. p., analysis, and production of benzoic acid by alkaline hydrolysis agree with those reported by Naylor and Dyer (*loc. cit.*), but in other respects our results are essentially different. On this account, the name oroxylin-A is suggested for our product, although it is probably identical with that of Naylor and Dyer.

We base our conclusions on the structure of oroxylin-A on the following observations : (a) It gives the magnesium–hydrochloric acid xanthoxine reaction; (b) the formula $C_{16}H_{12}O_5$ satisfies the analytical results as well as the $C_{19}H_{14}O_6$ formula of Naylor and

Dyer; (c) it contains one methoxyl group; (d) it forms a *diacetyl* and a dimethyl derivative and a monomethyl derivative which yields an oxonium platinichloride. These results indicate that it is a dihydroxymethoxyflavone, $C_{15}H_7O_2(OH)_2\cdot OMe$.

(e) It gives benzoic acid on alkaline hydrolysis, indicating that the 2-phenyl group is unsubstituted. (f) It does not contain a 3-hydroxyl group, since it is stable to aerial oxidation in alkaline solution. (g) It gives a reddish-violet coloration with alcoholic ferric chloride, unlike primetin (Nagai and Hattori, *Acta Phytochim.*, 1930, **5**, 1), which gives a green colour. It does not give a brown coloration with ammonium molybdate and acetic acid (cf. Quastel, *Analyst*, 1931, **56**, 311), nor does it reduce ammoniacal silver nitrate. Ortho-related hydroxyl groups are therefore absent. (h) On demethylation it gives demethyloroxylin-A, unchanged in m. p. by admixture with authentic baicalein (5 : 6 : 7-trihydroxyflavone; Shibata, Iwata, and Nakamura, *Acta Phytochim.*, 1923, **1**, 105; Bargellini, *Gazzetta*, 1919, **49**, ii, 47) kindly supplied by Prof. Shibata, to whom we express our best thanks. In all probability, therefore, oroxylin-A is 6-*O*-methyl baicalein (5 : 7-dihydroxy-6-methoxyflavone) (I). This is confirmed by the identity of its mono- and di-methyl derivative with 5-hydroxy-6 : 7-dimethoxyflavone and 5 : 6 : 7-trimethoxyflavone respectively (Bargellini, *loc. cit.*). The synthesis of (I) is in progress.



(I.)

EXPERIMENTAL.

Improved Method for the Extraction of Oroxylin-A (*5 : 7-Dihydroxy-6-methoxyflavone*).—Dried powdered root-bark of *Oroxylin indicum*, Vent, was extracted with acetone and the extract was concentrated and added to an equal volume of 50% alcohol. The precipitate on repeated crystallisation from alcohol gave yellow needles, m. p. 231—232°. Yield, 0·86%. Thus obtained, oroxylin-A dissolves in alkali solution with a red colour which rapidly changes to green. This behaviour is due to the presence of a trace of impurity, for after removal of the green flocculent precipitate and acidification of the filtrate the oroxylin-A obtained has the same m. p. but now dissolves in alkali to a yellow solution which is stable to aerial oxidation. The behaviour of the impurity in alkali corresponds to that of baicalein (5 : 6 : 7-trihydroxyflavone; Bargellini, *loc. cit.*) [Found for oroxylin-A : C, 67·7; H, 4·1; OMe, 10·2. Calc. for $C_{15}H_9O_4(OMe)$: C, 67·6; H, 4·2; OMe, 10·9%]. With magnesium and hydrochloric acid in aqueous-alcoholic solution, it gives an orange-red colour. *Diacetyloroxylin-A* (*5 : 7-diacetoxy-6-methoxyflavone*) (acetic anhydride–anhydrous sodium acetate) separated from alcohol in colourless needles, m. p. 131—132° (Found : C, 65·0; H, 4·4. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4%), insoluble in alkali and giving no coloration with alcoholic ferric chloride. Naylor and Dyer's supposed triacetyl derivative is stated to melt at 150—152°. *Monobenzoyloroxylin-A* (*5-hydroxy-7-benzoyloxy-6-methoxyflavone*) (benzoyl chloride–pyridine) separated from alcohol in pale yellow needles, m. p. 210° (Found : C, 71·4; H, 4·3. $C_{23}H_{16}O_6$ requires C, 71·1; H, 4·1%), insoluble in dilute alkali solution and giving a violet coloration with alcoholic ferric chloride indicating a 5-hydroxy-group. Dibenzoylation was attempted without success.

Monomethyloroxylin-A (diazomethane–acetone–ether solution) corresponds in properties and analysis to 5-hydroxy-6 : 7-dimethoxyflavone (Bargellini, *loc. cit.*). This product was also obtained with methyl sulphate and 10% alkali at 40°. The *platinichloride* separated from acetic acid–hydrochloric acid in deep yellow needles, m. p. 185—187° (decomp.). The crystals were dried at 105° [Found: Pt, 20·1. $(C_{17}H_{14}O_5)_2,H_2PtCl_6$ requires Pt, 19·4%]. *Acetylmonomethyloroxylin-A* (*5-acetoxy-6 : 7-dimethoxyflavone*) (acetic anhydride–anhydrous sodium acetate) separated from alcohol in colourless needles, m. p. 130—131° (Found : C, 66·8; H, 4·7. $C_{19}H_{16}O_6$ requires C, 67·0; H, 4·7%). *Benzoylmethyloroxylin-A* (*5-benzoyloxy-6 : 7-dimethoxyflavone*) (benzoyl chloride–pyridine) separated from acetone in colourless cubes, m. p. 206—207° (Found : C, 71·5; H, 4·7. $C_{24}H_{18}O_6$ requires C, 71·9; H, 4·5%). Both compounds were insoluble in dilute alkali solution and gave no ferric chloride reaction. Dimethyloroxylin-A was obtained from the monomethyl derivative (0·1 g.) by treatment with methyl sulphate (3 c.c.) and 20% potassium hydroxide solution (3 c.c.) in boiling acetone; it corresponds in properties and analysis to 5 : 6 : 7-trimethoxyflavone (Bargellini, *loc. cit.*).

Hydrolysis of Oroxylin-A.—The substance (0·2 g.), dissolved in 10% potassium hydroxide solution (14 c.c.), was heated at 100° in a sealed tube for 8 hours. The resulting alkaline solution was extracted with ether, again after saturation with carbon dioxide, and a third time after

acidification with hydrochloric acid. The viscous residue obtained from the first extract smelt strongly of acetophenone and did not give the benzaldehyde test with alkaline silver nitrate. The second extract yielded nothing; the third gave benzoic acid. Hydrolysis of methyloroxylin-A with methyl-alcoholic potash also gave benzoic acid. *Demethylation of Oroxylin-A.*—A mixture of oroxylin-A (0·2 g.), acetic anhydride (5 c.c.), and hydriodic acid (*d* 1·27; 5 c.c.) was refluxed at 145—150° (oil-bath) for 2 hours and poured into saturated sodium hydrogen sulphite solution. The precipitate on successive recrystallisation from alcohol, glacial acetic acid, and xylene had m. p. 265—266°, not depressed by authentic baicalein (5 : 6 : 7-trihydroxyflavone), to which it corresponded also in properties and analysis.

All the analyses except the methoxyl determination of oroxylin-A are micro-determinations by Dr. Schoeller.

The authors thank Lt.-Col. S. S. Sokhey, I.M.S., Director of the Haffkine Institute, Bombay, for providing facilities for most of the work, Dr. K. S. Mhaskar, who suggested the problem, for his interest and help, and Prof. D. B. Limaye of the Ranade Institute, Poona, for his helpful criticism.

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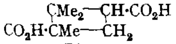
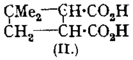
132. *The Synthesis of* cis- *and* trans-dl-*Norcaryophyllenic Acids and of Dehydronorcaryophyllenic Acid.*

By H. N. Rydon.

A liquid dibasic acid, $C_9H_{14}O_4$, was isolated by Semmler and Mayer (*Ber.*, 1911, **44**, 3157) from the product of ozonolysis of the mixture of sesquiterpenes known as caryophyllene. They named it "caryophyllenic acid" and assigned to it the structure (I) which represents it as a methylnorpinic acid. Deussen and Hacker (*J. pr. Chem.*, 1929, **122**, 261) threw a certain amount of doubt on this formula by the isolation of a "dibromocaryophyllenic acid." The position was further complicated by the work of Ruzicka, Bardhan, and Wind (*Helv. Chim. Acta*, 1931, **14**, 423), who not only separated Semmler's acid into two fractions —an acid, $C_9H_{14}O_4$, m. p. 66—75°, and a homologue, $C_8H_{12}O_4$, m. p. 145—150°—but showed that the glycols obtained from the former by the action of phenylmagnesium bromide and of methylmagnesium iodide gave different products on oxidation.

Experiments were undertaken to synthesise an acid of structure (I) in order to compare it with the product from natural sources. While the work was in progress Evans, Ramage,


(I.)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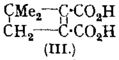
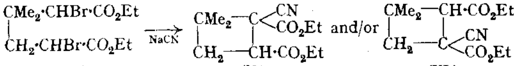

(III.)

and Simonsen (J., 1934, 1806) isolated caryophyllenic acid, $C_9H_{14}O_4$, m. p. 80—81°, and *d*-norcaryophyllenic acid, $C_8H_{12}O_4$, m. p. 125—127°, in a pure condition; they also converted the latter into dehydronorcaryophyllenic acid, $C_8H_{10}O_4$, m. p. 193°. Ruzicka and Zimmermann (*Helv. Chim. Acta*, 1935, **18**, 219) confirmed these results and tentatively assigned the structure (II) to norcaryophyllenic acid. Ramage and Simonsen (*Chem. and Ind.*, 1935, **54**, 151) then showed, by oxidative experiments, that this structure must be the correct one and also that dehydronorcaryophyllenic acid must be (III). Further work (Ramage and Simonsen, J., 1935, 532) proved conclusively that caryophyllenic and norcaryophyllenic acids were directly related, a point that had previously been assumed.

In view of these results it was decided to abandon the attempts to synthesise (I) and to direct attention to the synthesis of (II) and (III); it is with this work that the present paper is chiefly concerned.

Ethyl αα'-dibromo-ββ-dimethyladipate (IV) was cyclised to the *cyano*-ester (V or VI) by the method of Fuson and Kao (*J. Amer. Chem. Soc.*, 1929, **51**, 1536); acid hydrolysis of the product afforded a gum, which on treatment with concentrated hydrochloric acid yielded

dl-trans-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic acid (II), m. p. 148—149°, not depressed * by the *dl*-norcaryophyllenic acid obtained as a by-product in the preparation of the dehydro-acid (Ramage and Simonsen, *loc. cit.*); furthermore, (II) was readily converted by the method of Evans, Ramage, and Simonsen (*loc. cit.*) into 3 : 3-dimethyl-Δ^1-*cyclo*butene-1 : 2-dicarboxylic acid (*III*), m. p. 195°, unchanged * by authentic dehydronorcaryophyllenic acid.



(IV.) (V.) (VI.)

Treatment of the crude hydrolysis product with acetic anhydride yielded a liquid anhydride, which on digestion with water afforded *dl-cis*-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic acid (II), m. p. 149—150°, depressed to 118—120° by the *trans*-acid. This *cis*-acid was readily acted upon by acetyl chloride with the formation of *dl-cis*-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic anhydride, m. p. 40—41°; a mixture of this anhydride with the norcaryophyllenic anhydride of Ruzicka and Zimmermann (*loc. cit.*) melted at 39—41°.

These experiments thus confirm the structures (II) and (III) for norcaryophyllenic and dehydronorcaryophyllenic acid, respectively, so affording a synthetic proof of the rather unexpected presence in caryophyllene of a *gem*-dimethyl*cyclo*butane ring linked to another ring by adjacent carbon atoms.

A few points in the stereochemistry of norcaryophyllenic acid seem worthy of note. Three norcaryophyllenic acids have been described, one *d*-acid and two *dl*-acids. From the work here described, it seems probable that the acid, m. p. 148—149°, described as "*dl-cis*-norcaryophyllenic acid" by Ramage and Simonsen (J., 1935, 533) is in reality the *dl-trans*-acid, although the facile formation of an anhydride is certainly surprising. The *dl*-acid, m. p. 149—150°, described by Ruzicka and Zimmermann (*loc. cit.*) is, owing to the identity of its anhydride with the *dl-cis*-anhydride here described, almost certainly the *dl-cis*-acid.

It cannot, perhaps, be concluded with so much certainty that the naturally occurring *d*-acid has the *cis*-configuration, although the action of acetyl chloride at low temperatures in yielding a liquid anhydride which regenerates the parent acid, whereas acetic anhydride at high temperatures leads to the *dl-cis*-anhydride here described, seems to be considerable evidence in favour of this view. The *cis*-configuration is only to be expected, since, in the parent sesquiterpene, the *cyclo*butane and the *cyclo*hexane ring are most likely to be locked in the considerably less strained *cis*-position. If these configurations be accepted, it is evident that inversion in the sense *cis* ⟶ *trans* occurs during bromination in the preparation of the dehydro-acid; this is not unlikely if bromination is assumed to proceed through an intermediate enolic phase (Lapworth, J., 1904, 85, 30). These points can, however, only be settled by further work, in particular the resolution of both the *cis*- and the *trans*-acid and a more thorough study of their relationship to one another; this work is actively in hand.

Neither α-*iso*propyl- nor α-iso*butyl-glutaric acid* could be oxidised to a hydroxy- or a lactonic acid, although Lawrence (J., 1899, 75, 529) was able to oxidise β-*iso*propylglutaric acid to terpenylic acid by means of chromic acid, and Linstead and Rydon (J., 1933, 585) readily obtained δ-*iso*heptolactone by the oxidation of *iso*heptoic acid with alkaline permanganate; neither of these methods was successful when applied to the above α-*iso*-alkylglutaric acids.

Experimental.

The preparation of ββ-dimethyladipic acid by the oxidation of 3 : 3-dimethyl*cyclo*hexanone was a matter of some difficulty, since, contrary to Crossley and Renouf (J., 1905, 87, 1496), a mixture of acids was produced. The following method is an improvement of Blanc's process (*Bull. Soc. chim.*, 1905, 33, 898). A warm solution of 136 g. of ββ-dimethylglutaric anhydride in 1100 c.c. of calcium-dried absolute alcohol was added as fast as possible (25 minutes) to 180 g.

* The identity of these products has been independently confirmed by Prof. J. L. Simonsen, F.R.S.

of sodium. After being kept for 30 minutes at room temperature, the mixture was heated at 140—150° over-night and allowed to cool to 100°, and the alcohol distilled off while 1200 c.c. of water were slowly added; the residue was strongly acidified and steam-distilled. The distillate (2·5 l.) was saturated with ammonium sulphate and extracted with ether. Distillation of the dried extract from two such experiments yielded 187 g. (76%) of ββ-dimethyl-δ-valerolactone, b. p. 118—120°/20 mm., 89—90°/1·5 mm., m. p. 29°. ββ-Dimethyladipic acid was prepared from this lactone by Blanc's method (*Bull. Soc. chim.*, 1908, 3, 291).

Ethyl αα'-Dibromo-ββ-dimethyladipate.—11 G. of ββ-dimethyladipic acid (m. p. 86—88°) were treated with 17·5 g. of thionyl chloride and heated on the steam-bath for 1 hour, 22 g. of bromine added drop by drop, and the whole heated over-night, poured into 80 c.c. of absolute ethyl alcohol, refluxed for 30 minutes, and poured into water. Extraction with ether, followed by drying and distillation, afforded 18 g. (75%) of *ethyl αα'-dibromo-ββ-dimethyladipate*, b. p. 178—182°/12 mm. (Found: Br, 41·6. $C_{12}H_{20}O_4Br_2$ requires Br, 41·2%).

3 : 3-*Dimethyl*cyclo*butane*-1 : 2-*dicarboxylic Acid.*—18 G. of ethyl dibromodimethyladipate were refluxed for 24 hours with 8 g. of sodium cyanide suspended in 15 c.c. of calcium-dried ethyl alcohol. The dark brown liquid was filtered and distilled. The product (11 g.), b. p. 135—137°/2 mm., was impure (Found: N, 2·7. Calc. for $C_{12}H_{19}O_4N$: N, 5·5%) and no successful method of purification has yet been devised. It was hydrolysed and decarboxylated by refluxing for 12 hours with 50 c.c. of concentrated hydrochloric acid. The cooled solution was exhaustively extracted with ether, evaporation of the dried extract affording 8 g. of a thick gum. 3 G. of this were heated with 15 c.c. of concentrated hydrochloric acid over-night at 180° in a sealed tube. The product (decolourised with charcoal) on evaporation yielded *dl-trans*-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic acid, which crystallised from benzene (in which it was very sparingly soluble) in minute clusters of prisms, and from water in small needles, m. p. 148—149° (Found: C, 55·5; H, 6·9. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 7·0%).

A further 10 g. of the crude acid, prepared as described above, were heated at 220° in a sealed tube for 6 hours with 30 c.c. of acetic anhydride. On distillation 3 g. of anhydride were obtained as a thick oil, b. p. 98—100°/0·8 mm. This was digested with water and, on evaporation to dryness, followed by two recrystallisations from water, yielded 0·64 g. of *dl-cis*-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic acid in prisms, m. p. 149—150° (Found: C, 55·6; H, 7·1. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 7·0%).

0·45 G. of the *cis*-acid was treated with 4·5 c.c. of acetyl chloride. Reaction commenced in the cold and was completed by gentle refluxing for 1½ hours. Distillation afforded 0·24 g. of *dl-cis*-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic anhydride as a colourless oil, b. p. 100—102°/1 mm., which solidified; m. p. 40—41° (Found: C, 62·3; H, 6·6. Calc. for $C_8H_{10}O_3$: C, 62·3; H, 6·5%).

3 : 3-*Dimethyl*-Δ^1-cyclo*butene*-1 : 2-*dicarboxylic Acid.*—0·5 G. of the synthetic *dl-trans*-acid was treated with 1·25 g. of phosphorus pentachloride and heated on the water-bath for 10 minutes. The product was heated over-night at 140° in a sealed tube with 0·5 g. of bromine, and the whole poured into 10 c.c. of methyl alcohol and refluxed for 1 hour; it was then treated with water, and the bromo-ester isolated with ether. Without distillation, this was refluxed with 1 g. of potassium hydroxide in 2 c.c. of ethyl alcohol for 2 hours. The product was diluted considerably with water, the alcohol driven off on the water-bath, the residue extracted with ether, and the product (after drying and removal of ether) triturated with concentrated hydrochloric acid; the insoluble portion (m. p. 140—150°), on crystallisation from water afforded leaflets of 3 : 3-dimethyl-Δ^1-*cyclo*butene-1 : 2-dicarboxylic acid, m. p. 195° (Found: C, 56·7; H, 6·35. Calc. for $C_8H_{10}O_4$: C, 56·5; H, 5·9%).

Miscellaneous Experiments.—α-iso*Propylglutaric acid.* The following is an improvement of Heinke and Perkin's method (J., 1896, 69, 1507). To a solution of 11·5 g. of sodium in 200 c.c. of absolute alcohol, 101 g. of ethyl *iso*propylmalonate were added followed by 69 g. of ethyl β-chloropropionate. The mixture was refluxed over-night and then worked up in the usual manner. Ethyl α-carbethoxy-α-*iso*propylglutarate (31 g.), b. p. 140—145°/2·5 mm., was refluxed for 3 days with 90 c.c. of formic acid, 25 c.c. of water, and 30 c.c. of concentrated sulphuric acid. α-*iso*Propylglutaric acid (15·5 g.; 89%) separated on cooling and was recrystallised from benzene–petroleum (b. p. 60—80°), forming clusters of prisms, m. p. 94—95°.

α-iso*Butylglutaric acid.* By the treatment described above, 108 g. of ethyl *iso*butylmalonate yielded 40 g. (26%) of ethyl α-carbethoxy-α-*iso*butylglutarate, b. p. 150—155°/2 mm., hydrolysis of which (24 hours) produced 21 g. (88%) of *α-isobutylglutaric acid*, m. p. 68° after crystallisation from light petroleum (Found: C, 57·4; H, 8·65. $C_9H_{16}O_4$ requires C, 57·4; H, 8·5%).

Products from γ-carboxy-γ-isoheptolactone. (1) Saturation of a solution of 12 g. of the lactonic

acid in 100 c.c. of absolute alcohol with hydrogen bromide at 0° afforded only the bromine-free lactonic ester, b. p. 147—148°/12 mm., $n_D^{20°}$ 1·4500, $d_{4°}^{20°}$ 1·0952, $[R_L]_D$ 49·08 (calc., 49·49). (2) 11 G. of the lactonic acid were mixed with 83 g. of phosphorus pentabromide and 20 g. of phosphorus tribromide; after 12 hours, the mixture was poured into alcohol. The product (23 g.), b. p. 145—150°/15 mm., deposited crystals; these, recrystallised from light petroleum (b. p. 60—80°), had m. p. 126—127° (Found: Br, 38·0. $C_7H_{11}O_2Br$ requires Br, 38·6%) and were not further investigated. Distillation of the filtrate yielded *ethyl* α-*bromo*-α-iso*propylglutarate*, b. p. 138—142°/11 mm. (Found: Br, 25·2. $C_{12}H_{21}O_4Br$ requires Br, 25·9%).

The author is indebted to Prof. L. Ruzicka for a specimen of norcaryophyllenic anhydride, to Prof. J. L. Simonsen, F.R.S., for a specimen of norcaryophyllenic acid and still more for his interest and encouragement, and to the Royal Society for a grant.

IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, January 24th,* 1936.]

133. *Polycyclic Aromatic Hydrocarbons. Part XIV. A New Synthesis of 3 : 4-Benzphenanthrene.*

By C. L. HEWETT.

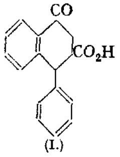
THE fact that 3 : 4-benzphenanthrene is one of the few carcinogenic compounds not related to 1 : 2-benzanthracene makes it desirable to extend investigation to a variety of simple derivatives in order to ascertain whether the cancer-producing activity of 3 : 4-benzphenanthrene is fortuitous or whether it is a property commonly associated with this type of molecular structure. In this connexion it is of interest that the three unknown pentacyclic hydrocarbons composed entirely of six-membered benzenoid rings all contain the ring system of 3 : 4-benzphenanthrene (for formulæ, see Barry, Cook, Haslewood, Hewett, Hieger, and Kennaway, *Proc. Roy. Soc.*, 1935, *B*, **117**, 328).

In the method already recorded for the synthesis of 3 : 4-benzphenanthrene (Cook, J., 1931, 2524) the formation of this ring system by a Pschorr reaction is accompanied by considerable cyclisation to the benzanthracene structure in spite of the fact that the latter requires ring closure at a β-position of the naphthalene system of a molecule in which a free α-position is also available for ring closure. This indicates a resistance to formation of the 3 : 4-benzphenanthrene system, which is probably best interpreted as due to steric factors. The present communication describes a new synthetic route to 3 : 4-benzphenanthrene which has the advantage that no alternative mode of cyclisation is possible. Moreover, the new method should be more readily adaptable to the synthesis of benzphenanthrene homologues, one of which is now described, and it is hoped, also, to utilise the same type of method for the synthesis of 1 : 2 : 5 : 6-dibenzphenanthrene.

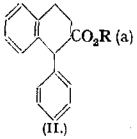
The new method is based on the observation of Haworth and Sheldrick (J., 1935, 637) that diphenylmethylsuccinic acids (obtained by reduction of the diphenylitaconic acids arising from the condensation of benzophenones with ethyl succinate) may be cyclised to phenyltetralone derivatives, whereas Stobbe and Vieweg (*Ber.*, 1902, **35**, 1727) had shown that diphenylitaconic acid is cyclised to an indone derivative. The former authors did not investigate the parent diphenylmethylsuccinic acid, but it has now been found that its anhydride undergoes the expected cyclisation with aluminium chloride to *4-keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid* (I). This was reduced by Clemmensen's method to *1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid* (IIa; R = H), the *ethyl* ester of which was reduced by sodium and alcohol to *1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthylcarbinol* (IIb).

The Grignard compound of *1-phenyl-2-chloromethyl-1 : 2 : 3 : 4-tetrahydronaphthalene* (IIc), obtained from the carbinol (IIb) by means of thionyl chloride and dimethylaniline, reacted with carbon dioxide at − 15° to give a 67% yield of *1-phenyl-1 : 2 : 3 : 4-tetrahydro-naphthyl-2-acetic acid* (IId; R = H). In this reaction there were obtained as by-products 1-phenyl-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (IIe) and *αβ-bis-(1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthyl)ethane*. The acid (IId; R = H) was either sulphonated or un-

affected by treatment at 100° with sulphuric acid of various concentrations, but was converted into *2-keto-1 : 2 : 9 : 10 : 11 : 12-hexahydro-3 : 4-benzphenanthrene* (III) by the

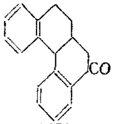


(I.)

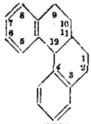


(II.)

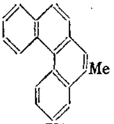
(b) $CH_2 \cdot OH$
(c) CH_2Cl
(d) $CH_2 \cdot CO_2R$
(e) CH_3



(III.)



(IV.)



(V.)

action of aluminium chloride on its chloride. When the reaction was carried out at 0° much acid chloride was unchanged, but complete reaction was effected by heating on the water-bath. This contrasts with the behaviour of 2-phenyl*cyclo*hexylacetic acid (Cook, Hewett, and Lawrence, this vol., p. 77), which is cyclised with the utmost facility, and provides another illustration of the greater difficulty of formation of the 3 : 4-benzphenanthrene system.

The ketone (III) was reduced by the Kishner–Wolff method to *1 : 2 : 9 : 10 : 11 : 12-hexahydro-3 : 4-benzphenanthrene* (IV), which on dehydrogenation with platinum-black gave 3 : 4-benzphenanthrene in 60% yield. Although the stages are somewhat numerous, the yields are good throughout, so that the over-all yield of benzphenanthrene is 7·3% with respect to the diphenylmethylsuccinic acid. It is hoped to determine the configuration of the tetracyclic compounds (III and IV) by *X*-ray crystallographic examination.

The ketone (III) reacted normally with methylmagnesium iodide to give a crude carbinol, which was dehydrated with potassium hydrogen sulphate. The resulting hydrocarbon was dehydrogenated to *2-methyl-3 : 4-benzphenanthrene* (V), the biological testing of which and of the new specimen of 3 : 4-benzphenanthrene will be described elsewhere.

Experimental.

4-Keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic Acid (I).—Diphenylmethylsuccinic acid (43 g.) (Stobbe, *Annalen*, 1899, **308**, 100) was refluxed with acetyl chloride (45 c.c.) for 2 hours; all the acid had then dissolved. The excess of acetyl chloride and the acetic acid were removed at the pressure of the water-pump and the residue was dissolved in nitrobenzene (50 c.c.) and slowly added to an ice-cold solution of aluminium chloride (43 g.) in nitrobenzene (250 c.c.). After being kept for 20 hours at 0°, the solution was decomposed with ice and hydrochloric acid, the nitrobenzene distilled with steam, and the residue dissolved in dilute sodium carbonate, filtered, and acidified. The *keto-acid* (I) crystallised from acetic acid in almost colourless tablets (29 g.), m. p. 208—209° (Found: C, 76·5; H, 5·35. $C_{17}H_{14}O_3$ requires C, 76·65; H, 5·3%). The *ethyl* ester, prepared by refluxing the acid with five parts of alcoholic hydrogen chloride, crystallised from alcohol in colourless, slender, silky needles, m. p. 122—123° (Found: C, 77·6; H, 6·3. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·15%).

1-Phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic Acid (IIa; R = H).—This was obtained in poor yield together with much unchanged keto-acid by the ordinary Clemmensen reduction of (I); no better yields were obtained by using the ester. When anisole was used as a solvent and the crude reduced acid was esterified, the yield of distilled ester was 78%. The keto-acid (I) (65 g.), anisole (130 c.c.), water (264 c.c.), concentrated hydrochloric acid (132 c.c.), and amalgamated zinc (200 g.) were boiled under reflux for 5 hours, concentrated hydrochloric acid (33 c.c.) being added at the end of each hour. After cooling, the acid was extracted with ether, separated from

neutral products by solution in dilute sodium carbonate, and converted into the *ethyl* ester by refluxing with alcoholic hydrogen chloride. The ester (IIa; R = Et) (53 g.) distilled at 170—173°/0·8—1·0 mm. and crystallised from alcohol in colourless needles, m. p. 61—62° (Found: C, 81·0; H, 7·2. $C_{19}H_{20}O_2$ requires C, 81·35; H, 7·2%). Hydrolysis with alcoholic potash gave the *acid* (IIa; R = H), b. p. 200°/0·8 mm., which crystallised from *cyclo*hexane in irregular colourless rhombs, m. p. 148—148·5° (Found: C, 80·7; H, 6·3. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

1-*Phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylcarbinol* (IIb).—The ester (IIa; R = Et) (55 g.) was dissolved in ethyl alcohol (300 c.c.), and sodium (27 g.) added during ¾—1 hour. After the sodium had dissolved (2—3 hours), most of the alcohol was removed, the residue diluted with water (1 l.), and the precipitated solid extracted four times with ether. The ethereal solution was washed, dried, and distilled; the *carbinol* (IIb) (26 g.), b. p. 175—180°/1 mm., crystallised from aqueous alcohol and then from ligroin in light feathery needles, m. p. 93—94° (yield, 67%) (Found: C, 85·7; H, 7·65. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). The aqueous solution on acidification yielded 18 g. of acid, which was re-esterified and again reduced. In this way 60·5 g. of the carbinol and 10 g. of acid were obtained from 94 g. of the ester.

1-*Phenyl*-2-*chloromethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (IIc).—Thionyl chloride (12·5 g.) was slowly added to an ice-cold agitated solution of the alcohol (IIb) (22 g.) in carbon tetrachloride (40 c.c.) and freshly distilled dimethylaniline (14 g.). The mixtnre was kept for ½ hour in ice and for ½ hour on the water-bath; ice was added, and the carbon tetrachloride solution washed with dilute hydrochloric acid and dilute sodium carbonate, dried, and distilled. The *chloride* (IIc) (21 g. 90%), b. p. 168°/0·8 mm., crystallised from alcohol in colourless rhombs, m. p. 71—72° (Found: C, 79·5; H, 6·75. $C_{17}H_{17}Cl$ requires C, 79·5; H, 6·7%).

1-*Phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthyl*-2-*acetic Acid* (IId; R = H).—During 4 hours dry carbon dioxide was slowly passed into a Grignard reagent prepared from the aforesaid chloride (16 g.), magnesium (1·6 g.), and ether (70 c.c.), cooled to − 15°. In the preparation of the Grignard solution methylmagnesium iodide was necessary for activation. Ice and hydrochloric acid were then added, the ethereal solution washed with water, and the acid extracted with dilute sodium carbonate. After crystallising from dilute alcohol and then from ligroin, the *acid* (IId; R = H) formed colourless irregular plates (11 g.), m. p. 138—139° after slight previous sintering (Found: C, 81·5; H, 7·0. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%). The neutral fraction, isolated from the ether, was distilled at 150—160°/1 mm. The distillate was dissolved in methyl alcohol and kept at 0° for 2 days; 1-*phenyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (IIe) was then deposited in stout colourless rhombs (1·1 g.), m. p. 46—47° (Found: C, 91·9; H, 8·0. $C_{17}H_{18}$ requires C, 92·3; H, 7·7%). The residue from the distillation slowly crystallised; after recrystallisation from alcohol and then ligroin it had m. p. 169·5—170·5° and was shown by analysis to be αβ-*bis*-(1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthyl*)*ethane* (0·3 g.) [Found: C, 92·2; H, 7·8; *M* (Rast), 359. $C_{34}H_{34}$ requires C, 92·3; H, 7·7%; *M*, 442].

2-*Keto*-1 : 2 : 9 : 10 : 11 : 12-*hexahydro*-3 : 4-*benzphenanthrene* (III).—The acid (14 g.) was boiled with thionyl chloride (70 c.c.) for 1 hour, and the excess of thionyl chloride removed in a vacuum. The residue was dissolved in carbon disulphide (70 c.c.) and cooled in ice, aluminium chloride (14 g.) slowly added, and the mixture kept in ice for 4 hours; ice and hydrochloric acid were then added, together with some benzene to dissolve the sparingly soluble ketone. The benzene–carbon disulphide solution was washed with dilute aqueous sodium carbonate, dried, and evaporated. After crystallising from ethyl alcohol, the *ketone* (5·1 g.) formed almost colourless leaflets, m. p. 154—155° (Found: C, 86·8; H, 6·6. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%). The mother-liquors of the ketone on distillation gave a solid (7·4 g.), which crystallised from ice-cold methyl alcohol (in which it was easily soluble) in colourless needles, m. p. 55—56° (Found: C, 82·0; H, 7·5. $C_{20}H_{22}O_2$ requires C, 82·3; H, 7·55%). This was the *ethyl* ester (IId; R = Et) formed from some unchanged acid chloride. When ring closure of the acid chloride was effected by heating on the water-bath with aluminium chloride for 4 hours, the yield of ketone was increased to 70% and there was no unchanged acid. The *semicarbazone*, prepared by boiling the ketone with semicarbazide hydrochloride and sodium acetate in aqueous-alcoholic solution for 32 hours, crystallised from aqueous dioxan and had m. p. 235° (Found: N, 13·2. $C_{19}H_{19}ON_3$ requires N, 13·8%). The *oxime*, prepared in anhydrous pyridine, crystallised from alcohol in pale pink tablets, m. p. 191—192° (Found: C, 82·4; H, 6·6. $C_{18}H_{17}ON$ requires C, 82·1; H, 6·5%).

1 : 2 : 9 : 10 : 11 : 12-*Hexahydro*-3 : 4-*benzphenanthrene* (IV).—The semicarbazone of (III) (3 g.) was heated with sodium ethoxide (3 g. of sodium in 45 c.c. of ethyl alcohol) at 175—180° for 9 hours. After cooling, water was added, and the oil extracted with ether. The ethereal

layer was washed, dried, and evaporated, giving a crystalline solid (2·5 g.), which distilled at 148—153°/0·2 mm. After recrystallisation from alcohol, *hexahydrobenzphenanthrene* (IV) formed colourless rhombs, m. p. 47·5—48° (Found : C, 92·3; H, 7·8. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Dehydrogenation to 3 : 4-benzphenanthrene was effected by heating with platinum-black at 310—320° for 7 hours in an atmosphere of carbon dioxide. Purification was effected through the picrate, m. p. 123—125° (lit., 126—127°), and the regenerated hydrocarbon was distilled (60% yield), and crystallised from alcohol; m. p. 68° (lit., 68°). These m. p.'s were not depressed by specimens prepared by the method of Cook (*loc. cit.*).

2-Methyl-3 : 4-benzphenanthrene (V).—The Grignard reagent prepared from methyl iodide (2·5 g.; 3 mols.), magnesium (0·5 g.), and ether (15 c.c.) was cooled in ice and treated with finely powdered tetrahydrobenzphenanthrone (III) (1·5 g.). After ½ hour in ice the product was boiled for 1½ hours and cooled, and ice and ammonium chloride added. The ethereal solution, washed, dried, and evaporated, left a gum. Dehydration was effected by heating at 160° for 1 hour with potassium hydrogen sulphate (3 g.), and the non-crystalline hydrocarbon was dehydrogenated with platinum-black at 300—310° for 2 hours in a slow current of carbon dioxide. Distillation at 0·2 mm. from a bath at 210° gave a viscous oil (1·2 g.), of which the vermilion *picrate* crystallised from alcohol in needles, m. p. 132·5—133·5° (Found : C, 64·0; H, 3·5. $C_{19}H_{14},C_6H_3O_7N_3$ requires C, 63·7; H, 3·6%). The m. p. was depressed by 3 : 4-benzphenanthrene picrate. The pure picrate was shaken with ether and ammonia; the *hydrocarbon* (V), isolated by evaporation of the ether, crystallised from alcohol in small colourless leaflets, m. p. 69·5—70°, depressed by 3 : 4-benzphenanthrene (Found : C, 94·3; H, 5·75. $C_{19}H_{14}$ requires C, 94·2; H, 5·8%).

The author thanks Prof. J. W. Cook for the interest he has taken in this work.

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134. *The Mesomeric Effect of the Dimethylamino-group in Dimethylaniline, and the Nature of its Interaction with Halogen Groups.*

By RALPH J. B. MARSDEN and L. E. SUTTON.

THIS investigation was commenced in order to determine the electric dipole moment due to the " interaction " or " conjugation " of the dimethylamino-group with the benzene ring. As a qualitative test for the existence of such a moment, Ingold suggested (*Ann. Reports*, 1926, **23**, 140) that the sign of the moment of this group relative to the benzene ring should be determined. Later, a general, quantitative method of determining such moments was developed independently and applied by one of us (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668) to a number of groups : this is the method which is now used.* Its application requires a knowledge of the magnitudes and directions of the moments of corresponding aliphatic and aromatic compounds relative to some suitable common co-ordinates : the required moment is then the vector difference between the two. In order to determine the angle θ_2 between the moment of dimethylaniline and the C–N bond which links the group to the benzene ring the moments of dimethylaniline and its *p*-methyl, chloro-, bromo-, iodo-, and nitro-derivatives were measured : that of the *p*-amino-derivative has also been measured.

Another method for determining θ_2 has already been applied (Hertel and Dumont, *loc. cit.*), but it does not give an unambiguous answer; for instance, from the moments of dimethylaniline and of tetramethyl-*p*-phenylenediamine two possible angle values can be obtained by assuming that the groups rotate freely relative to one another and applying Williams's equation (*Z. physikal. Chem.*, 1928, *A*, **138**, 75) : by taking 1·58 and 1·23 as the respective moments (Fogelberg and Williams, *Physikal. Z.*, 1931, **32**, 27; Weissberger and Sängewald, *Z. physikal. Chem.*, 1929, *B*, **5**, 237), alternative values of approximately 33·5°

* After the experimental work had been completed, Hertel and Dumont (*Z. physikal. Chem.*, 1935, *B*, **30**, 139) reported measurements of several *p*-substituted dimethylanilines, but they did not use them for the purpose mentioned.

and 146·5° are found. It was anticipated that this ambiguity could be resolved, and the value of θ_2 checked, by the new data.

Those obtained and the results which they give are collected in Table I, which includes the data of other authors. The symbols used, *viz.*, μ_O, μ_S, and μ_T, represent the original, the substituent, and the total resultant moment respectively * (Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 562).

TABLE I.

Substituent group.	μ_S.	μ_T.	θ_2.	Substituent group.	μ_S.	μ_T.	θ_2.
H	—	1·58 *	—	Br	1·52	3·37 †	0°
		1·58 †	—			3·42 §	
		1·55 §		I	1·30	3·22 †	0
CH_3	0·4	1·29 †	38°	CN	3·97	5·90 §	0
		1·31 §		NO	3·14	6·9 ‡	0
Cl	1·56	3·29 †	0	NO_2	3·95	6·87 †	0
						6·15 §	

* Fogelberg and Williams, *loc. cit.*
† Present work.
‡ Le Fèvre and Smith, J., 1932, 2239.
§ Hertel and Dumont, *loc. cit.*

Clearly, some of these results must be abnormal, and it may be presumed that the anomalies arise from some kind of interaction between the groups (Höjendahl, "Studies of Dipole Moments," Copenhagen, 1928, p. 113; Bennett, *Ann. Reports*, 1929, **26**, 132; Hampson and Sutton, *loc. cit.*).

Of the substituent groups, the methyl group is least likely to interact with the dimethylamino-group, and therefore it is reasonable to take 38° as the best available value for θ_2. This agrees remarkably closely with the smaller of the two values from tetramethyl-*p*-phenylenediamine (33·5°), which fact indicates that any interaction between the dimethylamino-groups does not affect the rotating moments. As Dr. G. C. Hampson has pointed out to us, this might be expected, since such changes would affect the moments of the Ph–N bonds, which lie along the axis of rotation, rather than those of the CH_3–N bonds.

If now, in order to calculate the interaction moment, μ_e, of the dimethylamino-group with the benzene ring, triethylamine be taken as the aliphatic standard for comparison, and it be assumed that the three C–N bonds are mutually inclined at the tetrahedral angle, it follows that $\mu_{aliph.}$ is 0·9 and θ_1 is 109·5° while $\mu_{arom.}$ is 1·58 and θ_2 is 38°; μ_e is then found to be 1·55. This moment has the positive sign required in the case of an *op*-directing group, and, although its magnitude is admittedly rough, the comparison with calculated μ_e values for the amino-, hydroxy-, and methoxy-groups is interesting. These are 1·12, 0·84, and 1·03 respectively.† Thus μ_e is greater in aniline than in phenol, and greater in anisole or dimethylaniline than in the unmethylated compounds; furthermore, the increase when two methyl groups are introduced, as in $N(CH_3)_2$, 0·43, is greater than that when only one is introduced as in OCH_3, 0·19. These facts are parallel to the changes in chemical properties of the groups (Robinson, *Rapp. Inst. Intern. Chim. Solvay*, 1931, p. 423; Ingold, *Rec. trav. chim.*, 1929, **48**, 797). The explanation of the existence of these moments for various groups as a result of permanent "electromeric" effects which occur in *all* molecules of the unsaturated compounds was given in 1931 by one of us (Sutton, *loc. cit.*). The origin and cause of the "electromeric" effects were at that time obscure, but since then they have been explained as a result of wave-mechanical "resonance" between different structures; when some of these are highly polar an electromeric moment is generated

* Here and throughout, electric dipole moments are given in Debye units, *i.e.*, 10^{-18} e.s.u.

† These have been recalculated. The method for the hydroxyl group is that described previously (Sutton, *loc. cit.*), but some of the data are new: $\mu_{H_2O} = 1·84$, $\mu_{CMe_3 \cdot OH} = 1·66$, and $\mu_{PhOH} = 1·61$. For the methoxyl group, $\mu_{Me_2O} = 1·32$, $\theta_1 = 112°$ (Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473), $\mu_{PhOMe} = 1·23$, and $\mu_{p\text{-}C_6H_4Me \cdot OCH_3} = 1·20$ (whence $\theta_2 = 76°$) were taken. In treating the amino-group, the moment of N–H was calculated from $\mu_{NH_3} = 1·47$, the valency angles being assumed to be 109·5°, and thence μ_{NH_2}. The simplest solution to the problem of combining this with any value for μ_{CH_3N} to give the observed value of 1·23 for $CH_3 \cdot NH_2$ made $\theta = 90°$. Now, by taking $\mu_{PhNH_2} = 1·53$ and $\mu_{p\text{-}C_6H_4Me \cdot NH_2} = 1·27$ (whence $\theta_2 = 43° 29'$) the above value for μ_e is found. The moment values are taken from the table compiled by Sidgwick and collaborators (*Trans. Faraday Soc.*, 1934, **30**, appendix).

(Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789; Kumler and Porter, *J. Amer. Chem. Soc.*, 1934, **56**, 2549; Ingold, *Chem. Reviews*, 1934, **15**, 225). Robinson and Ingold have emphasised the view that the true determinant of the mode and ease of reaction of an organic molecule is the type and degree of resonance which occurs in a transient excited state of the molecule caused by approach of a molecule of the reagent. This they define as the " electromeric " effect proper, and they postulate that the " permanent electromeric effect," or mesomeric effect as Ingold has termed it, is relevant only in so far as it is a measure of the possible true " electromeric " effect.

Since, in the benzene derivatives, the mesomeric effect moments are only of the order of one-tenth of those of the highly polar structures (Sutton, *loc. cit.*), it is evident that the latter are of much higher energy content than the simple or classical structures, *i.e.*, they are excited structures, but that when the energy content of the molecule as a whole is increased by some activation process it is probable that these highly polar structures will become relatively more important. If, now, the mesomeric effect is greater in proportion for one compound than for another, it means that the energy levels of the excited polar structures lie closer to those of the classical structures in the former compound than they do in the latter, and therefore that they become relatively more important in the former than in the latter compound for a given amount of activating energy. Since the moments of the corresponding polar structures would all be approximately equal, it follows that it is likely that the mesomeric and electromeric effects are monotonically related. Whatever the reaction mechanism, the fact is that there is a qualitative relation between the *op*- or the *m*-directing powers of a group and the positive or negative magnitude of the mesomeric effect between it and the benzene ring.

It remains to discuss the interactions already remarked upon (p. 600). It has long been recognised that when a *m*-directing group is substituted para to an *op*-directing one, an anomaly due to interaction of some kind may appear, and those noted above with the nitro-, nitroso-, and cyano-groups are therefore only further examples of this.

The interactions with the halogens, which are themselves *op*-directing, are however of a type only recently discovered by Bennett and Glasstone (*Proc. Roy. Soc.*, 1934, *A*, **145**, 71; *Trans. Faraday Soc.*, 1934, **30**, 853), who pointed out that the data given by Bergmann and Tschudnowsky for the substituted anisoles clearly showed their existence. Sutton and Hampson (*Trans. Faraday Soc.*, 1935, **31**, 945) found interactions in diphenyl ethers also, and mentioned that the data of Bergmann and Tschudnowsky for the anilines (*Z. physikal. Chem.*, 1932, *B*, **17**, 100) provided further examples, whereas those for the phenols (Donle and Gehrckens, *ibid.*, **18**, 316) do not; this suggests that only the most powerful *op*-directing groups can produce them with the halogens. No marked interactions of either kind occur in the *p*-substituted toluenes.

In Table II, data relevant to interactions of both kinds are collected, and interaction moments ($\mu_{int.}$) are calculated in the following way. The moment of the compound is calculated on the assumption that no interaction occurs, the direction θ_2 of the " main " group moment being taken as that given by the moment of the *p*-methyl derivative: the interaction moment is then calculated as that moment, parallel to the axis passing through the two substituent-bearing carbon atoms of the benzene ring, which changes the calculated to the observed value. For example, the moment calculated for *p*-bromodimethylaniline, from the moments of dimethylaniline and bromobenzene (θ_2 being taken as 38°) is 2·95; the moment along the Br–C . . . C–N axis necessary to make this equal to the observed value, 3·37, is one of 0·45 with its negative end toward the bromine atom, *i.e.*, positive relative to the dimethylamino-group.

It will be noticed (i) that for a given substituent group the interaction moment decreases in the order $-NMe_2 > (-NH_2, -OPh, -OCH_3) > -OH$, *i.e.*, roughly in the order of decrease of *op*-directing power and of mesomeric moment of the groups; (ii) that the interaction moment is always positive relative to the main group for any of the substituent groups used; (iii) that, as pointed out by Bennett and Glasstone, for any one main group the interaction moment increases in the following order for substituent groups: $F < Cl < Br < I < NO_2$.

It may easily be shown that the large interactions are not due merely to mutual electrostatic polarisations of the groups by one another. Either of these polarisations may be

TABLE II.*

p-Substituent.	*Toluenes.* $\mu_{calc.}$	$\mu_{obs.}$	$\mu_{int.}$	*Phenols.* $\mu_{calc.}$	$\mu_{obs.}$	$\mu_{int.}$	*Anilines.* $\mu_{calc.}$	$\mu_{obs.}$	$\mu_{int.}$
F	—	—	—	—	—	—	2·74	2·75	0·01
Cl	1·96	1·95	−0·01	2·30	2·27	−0·03	2·87	2·93	0·06
Br	1·92	1·96	+0·04	2·27	2·18	−0·09	2·82	2·87	0·05
I	1·70	1·71	0·01	—	—	—	2·63	2·82	0·21
NO	—	—	—	(3·60)	4·72	+(1·12)	—	—	—
NO_2	4·35	4·42	0·07	4·34	5·04	0·71	5·17	6·2	0·95
CN	4·30	4·37	0·07	—	—	—	—	—	—
	Anisoles.			*Diphenyl ethers.*			*Dimethylanilines.*		
F	2·09	2·09	0·00	—	—	—	—	—	—
Cl	2·20	2·24	0·04	—	—	—	2·97	3·29	0·34
Br	2·17	2·30	0·15	—	—	0·17—0·19†	2·93	3·37	0·46
I	1·99	2·12	0·16	—	—	—	2·57	3·22	0·69
NO	—	—	—	—	—	—	(4·49)	6·90	(2·41)
NO_2	4·41	4·76	0·37	—	—	0·70—0·76†	5·04	6·87	1·86
CN	—	—	—	—	—	—	5·20	5·90	0·71

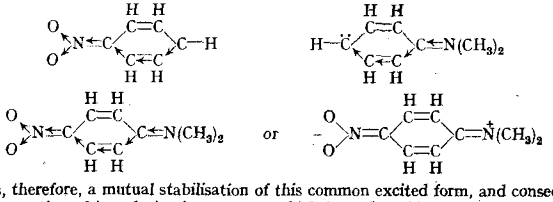
* The moment values used in performing these calculations were derived from the "Table c Dipole Moments" of Sidgwick and collaborators (*loc. cit.*) and are: for phenol, 1·61; p-cresol, 1·64 toluene, 0·40; aniline, 1·53; p-toluidine, 1·27; anisole, 1·23; p-tolyl methyl ether, 1·20; dimethyl aniline, 1·58; dimethyl-p-toluidine, 1·29; fluorobenzene, 1·42; chlorobenzene, 1·56; bromobenzene 1·52; iodobenzene, 1·30; benzonitrile, 3·97; nitrosobenzene, 3·14; nitrobenzene, 3·95.

† These are calculated by a different method and are taken from a paper by Sutton and Hampso (*loc. cit.*).

calculated separately with sufficient accuracy by a modification * of the method of Small wood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919), and the combined effect thu found. The moment induced in a group of refractivity 6—9 c.c. (*e.g.*, $-NO_2$, –Br) by on of 1·5 in the p-position, is of the order of 0·05—0·08; by one of 4, 0·13—0·21. In p-nitro dimethylaniline, where the two polarisations combine, an interaction moment of 0·35 a the most would be expected (${}_EP_{NMe_2}$ = 14·5 c.c.), not one of 1·86. In p-chlorodimethyl aniline the combined moments should be 0·15, instead of 0·34 as observed, and again i p-iododimethylaniline (${}_EP_I$ = 14 c.c.) the moment anticipated would be 0·20, not 0·69 That this method of calculation gives results of the right order in cases where probably n other effect occurs, is shown by the fact that the interaction calculated for p-nitrotoluene 0·15, agrees quite well with the observed value, 0·09.

The considerable residual abnormalities of moment are therefore to be attributed t mutual alteration of mesomeric effect.

In those compounds which have an *op*-directing group in the para-position to a *m*-directing group, the two groups are complementary to one another, since they both requir the same type of electron redistribution in the excited forms which are responsible for thei individual mesomeric effects, thus:



There is, therefore, a mutual stabilisation of this common excited form, and consequently an augmentation of its relative importance, which is made evident by the large positive

* The modification consists of making an allowance for the dielectric effect of the benzene ring which is interposed between the two groups. The factor $(\epsilon + 2)/3$, given by the Clausius and Mosotti model and employed, *e.g.*, by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171), is introduced; ϵ, the dielectric constant of the benzene ring, is taken to be 3.

interaction moment. This has, in essence, long been realised. It will be noticed that the interaction with the cyano-group is much less than that with the nitro-group, but that with the nitroso-group is almost as great; this order corresponds qualitatively to the relative *m*-directing powers of these groups (Robinson, *loc. cit.*; Ingold, *loc. cit.*; Hammick, New, and Sutton, J., 1932, 742).

In the case of the *p*-halogeno-amines and -ethers, both groups are *op*-directing, and consequently their mesomeric effects are not parallel but anti-parallel; not complementary but opposed. However, it may readily be seen that if one group is more powerfully directing than the other, the mesomeric effect of the weaker group may be diminished by that of the other, and then the direction of the interaction moment will be opposite to that of the normal mesomeric moment of the weaker group. In particular, if the dimethyl-amino-group reduces the mesomeric effect of the halogens, there will be generated an interaction of the same sign as that found with the *m*-directing groups, for a decrease of a positive electromeric effect (relative to the halogen, but negative relative to the dimethylamino-group) is equivalent to an increase of a negative one.

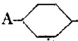
It has been pointed out to us by Dr. G. C. Hampson that increase or decrease of the relative importance of the excited, polar structures may be produced, not only by the similar or dissimilar requirements of valency arrangement therein by the two groups, but also by the fields of the groups, and that the two causes cannot easily be disentangled. What we may distinguish as the "valency" effects and the "polar" effects sometimes will act together and sometimes will not. Thus, in *p*-nitrodimethylaniline both effects favour an increased mesomeric effect: in *p*-iodonitrobenzene the "valency" effects augment one another, but whereas the field of the nitro-group augments the mesomeric effect of the iodo-group, that of the carbon–iodine dipole diminishes the mesomeric effect of the nitro-group somewhat; in *p*-iododimethylaniline the "valency" effects oppose, but the carbon–iodine dipole augments the mesomeric effect of the dimethylamino-group, while the moment of the latter group diminishes the mesomeric effect of the former. To discuss the question generally would be beyond the scope of this paper, but it is appropriate to consider the relative importance of the two effects in the particular cases under discussion. Dr. Hampson has suggested that the polar interaction in a compound A––B would be the algebraic difference $k(\mu_A\mu_{e_B} - \mu_B\mu_{e_A})$, μ being the moment of a group, μ_e its mesomeric moment, and k being a constant. Now, by inserting μ and μ_e values [the latter from a paper by one of us (Sutton, *loc. cit.*) or the present paper] and equating to the observed interaction moments, a value of k may be calculated which should include both the "polar" and the "valency" effects; k for the former effect should be universal, so large observed variations would indicate considerable "valency" effects. The results obtained for the dimethyl-anilines are given in Table III. The first set of k values were calculated without making allowance for the fact that the moment of the dimethylamino-group makes an angle of 38° with the Ph–N axis; the second set show the effect of making some allowance for this by taking the effective moment of the dimethylamino-group to be half its gross value. The differences are accentuated rather than diminished thereby.

TABLE III.

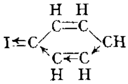
	k.			k.	
p-Chlorodimethylaniline ...	0·1015	0·118	*p*-Nitrodimethylaniline ...	0·248	0·273
p-Bromo ,, ...	0·133	0·159	*p*-Nitroso ,, ...	(0·459)	(0·502)
p-Iodo ,, ...	0·204	0·258	*p*-Cyano ,, ...	0·106	0·1115

The μ_e values used are admittedly rough, and it is impossible to say what value k should have; nevertheless, it seems a reasonable conclusion that in those cases where k is much greater than 0·1 there is probably a large "valency" effect in addition to any "polar" effect.

The conclusions that the iodo-compounds show such marked interactions and that these are due largely to valency effects give support to a hypothesis advanced by Robinson (J., 1933, 1114) that the ease of suppression of the mesomeric effect of a group depends upon its electrostatic deformation polarisability. Ingold (*loc. cit.*) has emphasised the converse, the importance of deformation polarisability in determining the mesomeric effect of a

group itself. It would not be expected that polarisability would be the sole determinant of mesomeric effect, for the rearrangement of bonds in the excited structures is not merely an electrostatic process; this is shown, *e.g.*, by the fact that, although the hydroxy- and the amino-group are less deformable than bromine, they produce greater mesomeric effects than it does. Therefore, we may consider that the mesomeric effect of a group depends upon two factors (in addition to the " polar " or " inductive " factor due to the moment of the group): the deformation polarisability, α, and what may be called a " bond type factor," χ, so that $\mu_e = \alpha\chi$. The process by which one group alters the mesomeric effect of another, through the " valency " effect, is by altering χ. Thus, if the *p*-substituent reduces χ for each of the halogens by the same amount, x, μ_e becomes $\alpha(\chi - x)$, and the abnormality, or interaction moment, is $-\alpha x$. Even if x is not constant, but decreases considerably from fluorine to iodine, α increases so rapidly in this order that it would still be possible for the interaction moment to increase in this, the observed, order.

It has been suggested by Klug (*J. Chem. Physics*, 1935, **3**, 747) that iu *p*-di-iodobenzene and *trans*-di-iodoethylene the iodine participates in excited structures of the type (I), wherein it has the same electronic structure as it has in the iodochlorides and similar compounds, *i.e.*, a decet in the fifth main quantum group. It is obviously possible that structures of this type might become importaut in compounds having a strong *op*-directing group para to the iodine atom, but even in *p*-iododimethylaniline, since the observed abnormality, 0·69, does not *exceed* the supposed mesomeric effect of the iodo-group itself, 0·86, we can only say that it is not essential to postulate this process, but that, nevertheless it may occur. The almost complete suppression of the mesomeric effect of the iodo-group should make the chemical properties of this compound of considerable interest.



(I.)

EXPERIMENTAL.

Determination of Electric Dipole Moments.—All measurements were made in benzene solution at 25·0° The dielectric constants were measured by the heterodyne apparatus previously described (Sutton, *loc. cit.*; cf. Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147). For some measurements the dilution condenser described by Sutton was used; for others, a single-solution condenser, essentially similar to the one described by Jenkins and Sutton (J., 1935, 609), but with a larger capacity, was used. Refractivities and densities were measured as before. The benzene density used in the calculations for any particular run was the value to which the density-f_2 curve extrapolated, since small variations were noticed.

Preparation and Purification of Materials.—*Benzene.* B.D.H. "A.R." Benzene was further pnrified by three fractional freezings and distillation from phosphoric oxide. Uniformity of samples was checked by f.p. determinations.

Dimethylaniline. A good commercial specimen (m. p. 1·85°) was refluxed for one hour with enough acetic anhydride to acetylate up to 10% by weight of monomethylaniline. The mixture was just neutralised with fairly dilute sodium carbonate solution, and steam-distilled. The distillate was extracted with ether, the extract dried and evaporated, and the product fractionated. The fraction, b. p. 191·5—194°, was dried over solid potassium hydroxide and again fractionated. The fraction, b. p. 193·0—193·4° (uncorr.; Anschütz)/753 mm., f. p. 2·35°, was retained and redistilled just before measurement; Perkin (J., 1896, **69**, 1207) gives b. p. 193° (corr.)/760 mm.; Beilstein gives f. p. 2·5°.

Dimethyl-p-*toluidine.* A commercial specimen was purified according to Hodgson and Kershaw (J., 1930, 277). The fraction, b. p. 207° (uncorr.) (cf. 207°, Hodgson and Kershaw, *loc. cit.*), obtained on fractionating the dried, ethereal extract of the steam-distillate, was used.

p-*Aminodimethylaniline.* *p*-Nitrosodimethylaniline, prepared from dimethylaniline (" Organic Syntheses," **2**, 17), was reduced by tin and hydrochloric acid (Wurster, *Ber.*, 1879, **12**, 523). The product was purified repeatedly by Wurster's method but retained a slight pink coloration; m. p. 38·5—39° (Wurster, *loc. cit.*, gives 41°).

p-*Chlorodimethylaniline.* A Sandmeyer reaction was performed with diazotised *p*-aminodimethylaniline (by Mr. J. Jackson). The product was recrystallised twice from ligroin (b. p. 40—60°) and once from ethyl alcohol; m. p. 33·5° (35·5°, Beilstein).

p-*Bromodimethylaniline.* Dimethylaniline was brominated directly, by Mr. J. Jackson, as directed by Weber (*Ber.*, 1875, **8**, 715; 1877, **10**, 763). The crude product, precipitated by alkali, was washed, and recrystallised four times from ethyl alcohol; m. p. 54·7° (55°, Weber, *loc. cit.*).

p-Iododimethylaniline was prepared by direct iodination of dimethylaniline (Weber, *ibid.*, p. 765; Baeyer, *ibid.*, 1905, **38**, 2762) in methyl-alcoholic solution at room temperature in the presence of mercuric oxide, the reaction being complete in a few minutes. The solution was greatly diluted with water and extracted with ether. The extract was concentrated somewhat and shaken several times with thiosulphate solution. This removed the violet substance which had already formed (Weber, *loc. cit.*) and reduced the tendency for its further formation, possibly by removing a catalyst. The extract was further concentrated, and the product thrice recrystallised from ligroin (b. p. 60—80°) (Norit), and then from ethyl alcohol. The m. p., 79—80·5° (corr.), was not altered by the final recrystallisation (Weber, *loc. cit.*, 79°; Baeyer, *loc. cit.*, 82°).

p-*Nitrodimethylaniline*. Two methods of preparation were used: (1) The reaction between trimethylamine and *p*-chloronitrobenzene (m. p. 83·5°; cf., 83°, Ssokolow, *Z. Chem.*, 1865, 602), as described by Leymann (*Ber.*, 1882, **15**, 1234); the product was recrystallised twice from ethyl alcohol; m. p. 164° (corr.). (2) To *p*-nitrosodimethylaniline (9 g.) in water (1 l.) was slowly added a solution of potassium permanganate (9 g.) in water (1·5 l.), and the manganese dioxide formed was removed by sulphur dioxide. The crude product was recrystallised successively from ethyl alcohol, ligroin–benzene, and ethyl alcohol; m. p. 164° (lit., 162—169°; many values near 164°). The purified product from the latter preparation was darker than that from the former, but they gave a mixed m. p. of 164°.

Polarisation Results.—The dielectric constant of benzene at 25·0° was taken as 2·2727 (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664; Sugden, J., 1933, 768, gives 2·272) and the refractive index as 2·2571 (obs.). The symbols have the same meaning as in previous papers from this laboratory.

The densities were not corrected for buoyancy, this having a negligible effect on the polarisations. The values marked * are interpolated or smoothed values.

Dimethylaniline.

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·04004	0·8781	2·4246	2·2668	92·6	41·2
0·02412	0·8764	2·3657	2·2632	93·9	41·3
0·02022	0·8759	2·3493	2·2618	93·1	41·1
0·01585	0·8754$_5$	2·3328	2·2612	93·2	41·4
0·00000	0·8737*	—	—	—	—

$^{\infty}P_2 = 93·6 \pm 0·5$ c.c.; $^{\infty}_{E}P_2 = 41·6$ c.c.;
$\mu = 1·58$.

p-*Aminodimethylaniline.*

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·02383	0·8792	2·3486	2·2688	85·9	46·4
0·01877	0·8780$_5$	2·3322	2·2662	85·7	46·3
0·01266	0·8766$_5$	2·3134	2·2631	86·5	46·1
0·00860	0·8757$_5$	2·3012	—	88·0	—
0·01261	0·8766$_5$	2·3142	2·2635	87·7	46·6
0·00910	0·8758	2·3022	2·2616	87·2	46·5
0·00616	0·8751$_5$	2·2928	—	87·4	—
0·00000	0·8738*	—	—	—	—

$^{\infty}P_2 = 88 \pm 1·0$ c.c.; $^{\infty}_{E}P_2 = 46·4$ c.c.;
$\mu = 1·42$.

p-*Bromodimethylaniline.*

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·00780	0·8799	2·3973	2·2609	271·9	49·8
0·00577	0·8781	2·3659	2·2602	276·3	51·0
0·00390	0·8767	2·3363	2·2587	279·8	48·7
0·00261	0·8755$_5$	2·3160	—	285·2	—
0·00000	0·8734*	—	—	—	—

$^{\infty}P_2 = 288·5 \pm 3·0$ c.c.; $^{\infty}_{E}P_2 = 49·8$ c.c.;
$\mu = 3·39$.

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·00975	0·8816	2·4280	2·2622	269·6	49·9
0·00713	0·8794	2·3872	2·2605	273·4	49·3
0·00483	0·8775	2·3509	2·2595	276·9	50·2

$^{\infty}P_2 = 284·1 \pm 1·0$ c.c.; $^{\infty}_{E}P_2 = 49·8$ c.c.;
$\mu = 3·36$.
μ (mean) $= 3·375$.

Dimethyl-p-*toluidine.*

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·04424	0·8778	2·3816	2·2680	79·4$_5$	46·6
0·01989	0·8756	2·3234	2·2624	80·7	46·8
0·01847	0·8754*	2·3190	2·2626	80·1	47·4
0·00936	0·8747	2·2970	2·2599	81·2$_5$	47·2
0·00000	0·8738*	—	—	—	—

$^{\infty}P_2 = 81·6$ c.c.; $^{\infty}_{E}P_2 = 47·0$ c.c.; $\mu = 1·29$.

p-*Chlorodimethylaniline.*

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·02186	0·8819	2·6121	2·2650	254·7	46·1
0·01676	0·8799	2·5349	2·2633	259·5	46·2
0·01125	0·8777	2·4492	2·2615	263·8	46·6
0·00756	0·8762$_5$	2·3955	2·2594	274·2	45·3

$^{\infty}P_2 = 274 \pm 1$ c.c.; $^{\infty}_{E}P_2 = 47$ c.c.; $\mu = 3·30$.

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·01203$_5$	0·8779	2·4595	2·2616	261·3	46·6
0·00909	0·8766	2·4144	2·2605	264·7	47·2
0·00610	0·8756$_5$	2·3678	2·2594	266·0	46·7
0·00000	0·8733*	—	—	—	—

$^{\infty}P_2 = 272 \pm 1$ c.c.; $^{\infty}_{E}P_2 = 47$ c.c.; $\mu = 3·29$.
μ (mean) $= 3·29_5$.

p-*Iododimethylaniline.*

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·01139	0·8877	2·4480	2·2654	264·8	56·9
0·00712	0·8825	2·3825	2·2626	267·3	57·4
0·00483	0·8793	2·3480	2·2607	269·9	56·3
0·00293	0·8772	2·3178	2·2594	269·6	59·0
0·00000	0·8735*	—	—	—	—

$^{\infty}P_2 = 272 \pm 2$ c.c.; $^{\infty}_{E}P_2 = 57 \pm 0·5$ c.c.;
$\mu = 3·22 \pm 0·02$.

p-*Nitrodimethylaniline.*

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_EP_2$.
0·00793	0·8777$_5$	2·7910	2·2657	900·6	56·8
0·00652	0·8770$_5$	2·7023	—	922·9	—
0·00589	0·8768	2·6635	2·2633	935·9	56·1
0·00396	0·8757	2·5380	2·2612	970·4	56·6
0·00324	0·8754	2·4878	—	970·2	—
0·00189	0·8744	2·3977	2·2590	983·9	56·0
0·00000	0·87375*	—	—	—	—

$^{\infty}P_2 = 1,035 \pm 5$ c.c.; $^{\infty}_{E}P_2 = 56·25$ c.c.;
$\mu = 6·87$.

SUMMARY.

The electric dipole moments of dimethylaniline and its *p*-methyl-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *p*-nitro-, and *p*-amino-derivatives have been measured in benzene solution at 25°: they are 1·58, 1·29, 3·29, 3·37, 3·24, 6·87, and 1·42 respectively.

The mesomeric effect of the dimethylamino-group and the benzene ring has been calculated to be 1·55.

The interaction moments between the dimethylamino-group and the substituent groups have been calculated on the assumption that that with the methyl group is zero: they are Cl 0·34, Br 0·46, I 0·69, and NO_2 1·86.

It has been shown that the dimethylamino-group reduces the mesomeric effect of the halogens, suppressing it almost completely in the iodo-derivative.

The nature and significance of mesomeric effects have been discussed.

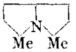
The authors wish to thank Prof. N. V. Sidgwick for his interest and advice, Dr. G. C. Hampson for permission to include certain material, Mr. J. Jackson for assistance with the preparations, and Imperial Chemical Industries Ltd. for a grant covering the cost of apparatus and materials.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, March 27th, 1936.*]

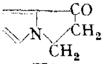
135. *The Lupin Alkaloids. Part IX. The Synthesis of 5 : 5′-Dimethyldi(1 : 2)pyrrolidine.*

By G. R. CLEMO and T. P. METCALFE.

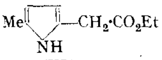
OF the structures for norlupinane consistent with the *n*-propyl *n*-amyl ketone obtained by Karrer and co-workers (*Helv. Chim. Acta*, 1928, **11**, 1062) from lupinine, two, *viz.*, octahydropyridocoline and methyloctahydropyrrocoline, have already been synthesised (J., 1932, 2959; 1935, 1743) and a third, 5 : 5′-*dimethyldi*(1 : 2)*pyrrolidine* (I), has now been prepared.



(I.)



(II.)

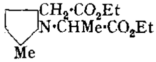


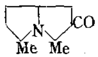
(III.)

The method used by Clemo and Ramage (J., 1931, 53) for the preparation of 3-keto-4 : 5-dihydrodi(1 : 2)pyrrole (II) was first tried, but it was not found possible to condense potassio-2-methylpyrrole with β-bromobutyronitrile.

Ethyl 2-methylpyrrole-5-acetate (III) was then prepared by the method used by Sohl and Shriner (*J. Amer. Chem. Soc.*, 1933, **55**, 3831) for the preparation of ethyl 1-methylpyrrole-5-acetate. The ester side chain was proved to be in position 5 by conversion into the dimethylpyrrole and degradation of this by means of hydroxylamine to acetonylacetonedioxime. The ester (III) was catalytically hydrogenated and condensed with ethyl α-bromopropionate, yielding *ethyl 2-methylpyrrolidine-5-acetate-*1*-α-propionate* (IV). The Dieckmann ring closure of this gave 4-*keto*-5 : 5′-*dimethyldi*(1 : 2)*pyrrolidine* (V), but the Clemmensen reduction of this gave the 4-*hydroxy*-compound. This result agrees with that recorded for the reduction of 3-keto-2-methyloctahydropyrrocoline in Part VIII (J., 1935, 1743), which also has a methyl group in the α-position to the carbonyl group. The Wolff reduction (*Annalen*, 1912, **394**, 86), however, gave 5 : 5′-dimethyldi(1 : 2)pyrrolidine as a colourless stable liquid.

(IV.)





(V.)

The stability of the bases increases in the order: octahydropyridocoline, methyloctahydropyrrocoline, 5 : 5′-dimethyldi(1 : 2)pyrrolidine, and there is a corresponding fall in their boiling points: 38—40°/1 mm.; 32—35°/1 mm.; 25°/1 mm.

Theoretically there should be eight stereoisomerides of the base (I), but in this work no evidence has been found of the occurrence of more than one form of (I), or of its derivatives such as (V).

EXPERIMENTAL.

Ethyl 2-Methylpyrrole-5-acetate.—Diazoacetic ester (7 g.) was added, with shaking, during ¼ hour to 2-methylpyrrole (9 g.) and copper-bronze (0·4 g.) at 100°, and the mixture kept at this temperature for a further hour. After filtration the dark brown liquid was distilled; 2-methylpyrrole (5·15 g.) was recovered, and *ethyl 2-methylpyrrole-5-acetate* (4·5 g.) obtained as a very pale yellow oil, b. p. 129—130°/12 mm. (Fonnd: C, 64·7; H, 7·5. $C_9H_{13}O_2N$ requires C, 64·7; H, 7·8%).

Ethyl 2-Methylpyrrolidine-5-acetate.—The pyrrole ester (9·4 g.), in a mixture of glacial acetic acid (20 c.c.) and ethyl alcohol (6 c.c.), was shaken for 36 hours with platinum oxide (0·5 g.) in hydrogen at 100 lb./sq. in. After filtration and removal of solvents, the residue was basified (50% potassium hydroxide solution), extracted with ether, and distilled, giving 7·7 g. of an oil, b. p. 98°/12 mm. (Found: C, 63·0; H, 9·8. $C_9H_{17}O_2N$ requires C, 63·2; H, 9·9%). The *picrate* formed yellow prisms, m. p. 112°, very soluble in alcohol, and the *picrolonate*, yellow prisms with oblique ends, m. p. 194° (Fonnd: C, 52·2; H, 6·0. $C_9H_{17}O_2N,C_{10}H_8O_5N_4$ requires C, 52·4; H, 5·7%).

Ethyl 2-Methylpyrrolidine-5-acetate-1-α-propionate.—The pyrrolidine ester (6·2 g.), α-bromopropionic ester (7·8 g.), and potassium carbonate (10 g.) were heated together on the water-bath for 5 hours. Water was added, and the oil extracted with ether, dried, and distilled (7·3 g., b. p. 150—151°/12 mm.) (Found: C, 62·0; H, 9·2. $C_{14}H_{25}O_4N$ requires C, 62·0; H, 9·2%).

4-*Keto*-5 : 5'-*dimethyldi*(1 : 2)*pyrrolidine.*—The di-ester (5·4 g.) was added to potassium (2 g.) powdered under xylene (15 c.c.). After the first vigorous reaction had abated, the whole was heated for 5 hours on the water-bath, alcohol added to dissolve unused potassium, then water (8 c.c.) and concentrated hydrochloric acid (50 c.c.), and the solution heated for 18 hours on the water-bath. After evaporation to dryness the residue was basified with potassium hydroxide solution (50%), and the *ketone* extracted with ether and distilled as a colourless oil (1·9 g., b. p. 65°/1 mm.) which became yellow after 2 hours (Found: C, 70·2; H, 9·9. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%). The *picrate* formed yellow needles, m. p. 186° (Found: C, 47·4; H, 4·4. $C_9H_{15}ON,C_6H_3O_7N_3$ requires C, 47·1; H, 4·7%), and the *picrolonate*, yellow rectangular prisms, m. p. 217° (Found: C, 54·9; H, 5·7. $C_9H_{15}ON,C_{10}H_8O_5N_4$ requires C, 54·7; H, 5·5%).

4-*Hydroxy*-5 : 5'-*dimethyldi*(1 : 2)*pyrrolidine.*—The ketone (0·5 g.) in concentrated hydrochloric acid (10 c.c.) was refluxed for 21 hours with amalgamated zinc (5 g.). The solution was then evaporated to dryness, and the residue basified with potassium hydroxide solution (50%) and steam-distilled. The distillate was acidified (hydrochloric acid) and evaporated to dryness, the residue basified with potassium hydroxide solution (50%) and extracted with ether, and the extract distilled (0·35 g., b. p. 68—70°/1 mm.) (Found: C, 69·6; H, 11·2. $C_9H_{17}ON$ requires C, 69·7; H, 11·0%). The *picrolonate* formed yellow lozenge-shaped crystals, m. p. 205° (Found: C, 54·5; H, 6·1. $C_9H_{17}ON,C_{10}H_8O_5N_4$ requires C, 54·4; H, 6·0%).

5 : 5'-*Dimethyldi*(1 : 2)*pyrrolidine.*—The ketone (2·4 g.) and hydrazine hydrate (1·6 g. of 95%) were refluxed for 15 hours, the hydrazone dried in ethereal solution, and the ether removed. The residue (1·2 g.) was heated at 160—180° for 11 hours in a sealed tube with sodium ethoxide (from sodium, 1·4 g., and absolute alcohol, 10 c.c.). Water (10 c.c.) and excess of hydrochloric acid were added, and the solution evaporated to dryness. The *base* was liberated by potassium hydroxide solution (50%), extracted with ether, dried, and distilled, yielding 0·65 g. of a colourless mobile liquid, b. p. 25°/1 mm. (Found: C, 77·9; H, 12·5. $C_9H_{17}N$ requires C, 77·7; H, 12·2%), which had a very penetrating odour and was easily soluble in water, giving a solution alkaline to litmus. The *picrate* formed yellow rectangular prisms, m. p. 249° (Found: C, 48·6; H, 5·5. $C_9H_{17}N,C_6H_3O_7N_3$ requires C, 48·9; H, 5·4%), and the *picrolonate*, stout brown prisms, m. p. 180° (Found: C, 56·8; H, 6·4. $C_9H_{17}N,C_{10}H_8O_5N_4$ requires C, 56·6; H, 6·2%).

Our thanks are due to the Royal Society for a grant.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.

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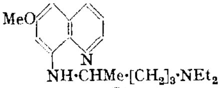
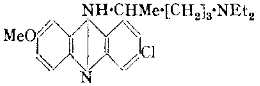
136. *The Synthesis of Substituted Acridines as Possible Antimalarial.*

By G. R. Clemo and W. Hook.

During recent years the magnitude and complexity of the malaria problem has been realise and in consequence a considerable amount of work has been done on the synthesis c possible antimalarial compounds. The best known and most valuable of such compound are the I.G. products plasmoquin (I) and atebrin (II).



(I.)



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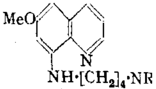


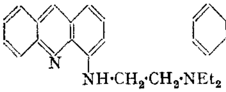
(III.)

Robinson and Baldwin (J., 1929, 2959; 1934, 1264) have prepared compounds relate to plasmoquin, and Robinson and Meisel (J., 1934, 1267) showed that the most effectiv compound of this type was 8-(δ-aminobutylamino)-6-methoxyquinoline (III; R = H Meanwhile Strukow and Magidson (*Arch. Pharm.*, 1933, **271**, 569) had prepared simila compounds with R = ethyl. Magidson and Grigorowsky (*Ber.*, 1936, **69**, 396) have als prepared compounds related to atebrin.

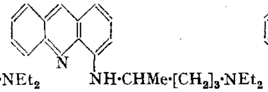
In consequence of the well-known antiseptic action of certain acridine derivatives an the fact that atebrin is an acridine derivative of which, at that time, the constitution wa generally unknown, it was thought desirable to synthesise compounds of acridine containin the characteristic basic centres and alkylamino-side chain of plasmoquin.

Compounds of 1-aminoacridine were decided upon, as the alkylamino-side chains woul then be in the same relative position to the heterocyclic nitrogen atom as in plasmoqui and related effective compounds. 1-(β-*Diethylaminoethylamino*)*acridine* (IV) has bee prepared by direct condensation of 1-aminoacridine and β-chloroethyldiethylamine, an also by condensing β-chloroethyldiethylamine with the *p*-toluenesulphonamide of 1-amino 5 : 10-dihydroacridine and subsequent hydrolysis of the resulting *p*-toluenesulphonamide.

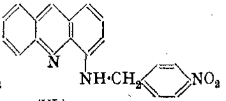
All attempts to prepare 1-(δ-diethylamino-α-methylbutylamino)acridine (V) in a simila manner have failed because of the ease with which δ-chloro-α-diethylaminopentane CH_3·CHCl·$[CH_2]_3$·NEt_2, loses the elements of hydrogen chloride in the presence of stron bases. δ-Chloro-α-diethylaminopentane could not be isolated in the free state, as i isomerised to give the ethochloride of 2-methyl-1-ethylpyrrolidine, isolated as the etho picrate; nor did it yield a crystalline hydrochloride, but a crystalline *methiodide* wa obtained and used in some of the condensation attempts.



(IV.)



(V.)



(VI.)

Attempted condensation of 1-chloroacridine and δ-amino-α-diethylaminopentane also failed to produce (V). 1-Aminoacridine has also been condensed with *p*-nitrobenzyl bromide to yield 1-(p-*nitrobenzyl*)*aminoacridine* (VI), and this has been reduced to the *amino*-compound, which gives a crystalline water-soluble dihydrochloride.

Experimental.

p-*Toluenesulphonamide of* 1-*Methylamino*-5 : 10-*dihydroacridine*.—The *p*-toluenesulphonamide of 1-amino-5 : 10-dihydroacridine (Clemo, Perkin, and Robinson, J., 1924, **125**, 179) (1 g.) was dissolved in 10 c.c. of 5% methyl-alcoholic potash and 5 c.c. of water, and 3 c.c. of

methyl sulphate added; a solid began to separate almost immediately. This (0·9 g.) crystallised from alcohol in stout yellow prisms, m. p. 170° (Found: C, 68·8; H, 5·7. $C_{21}H_{20}O_2N_2S$ requires C, 69·2; H, 5·5%).

1-*Methylaminoacridine.*—The above amide (2 g.) was dissolved in sulphuric acid (15 c.c.) and gave a cinnamon-coloured solution with an intense green fluorescence. After standing for 3 hours and heating on the water-bath for 1 hour, it was poured on ice, giving a red solution. On addition of excess of sodium carbonate, a yellow oil separated. This was taken up in ether, the ether removed, and the residue crystallised from light petroleum (b. p. 40—60°), giving fine orange prisms, m. p. 75° (Found: C, 80·6; H, 5·9. $C_{14}H_{12}N_2$ requires C, 80·8; H, 5·8%). The product was 1-*methylaminoacridine*, showing that during hydrolysis and subsequent working up, the 5 : 10-dihydro-compound had been oxidised to the acridine. These preparations were carried out as preliminaries to the following.

1-(β-*Diethylaminoethyl*)*aminoacridine* (IV).—1-Aminoacridine (4 g.), β-chloroethyldiethylamine hydrochloride (4 g.), and fused sodium acetate (2 g.) in alcohol (20 c.c.) were refluxed for 15 hours. The product was poured into water, excess of sodium carbonate added, and the oil which separated extracted with ether. Fractionation gave (IV) (6·4 g.) as a viscous, dark red oil, b. p. 180°/1 mm. (Found: C, 78·1; H, 7·9. $C_{19}H_{23}N_3$ requires C, 77·8; H, 7·85%). (IV) gives a *dipicrate*, dark red needles, m. p. 192° (Found: C, 49·5; H, 4·3. $C_{19}H_{23}N_3,2C_6H_3O_7N_3$ requires C, 49·5; H, 3·9%), and a *monopicrate*, scarlet prisms, m. p. 151° (Found: C, 57·5; H, 5·3. $C_{19}H_{23}N_3,C_6H_3O_7N_3$ requires C, 57·5; H, 5·0%). 1-Aminoacridine forms only a *monopicrate*, purplish-black plates, m. p. 220° (Found: C, 53·9; H 3·2. $C_{13}H_{10}N_2,C_6H_3O_7N_3$ requires C, 53·9; H, 3·1%).

The *dihydrochloride* of (IV) crystallised from moist acetone–methyl alcohol in dark red prisms, m. p. 104°, containing two molecules of water (Found: N, 10·5; Cl, 17·7. $C_{19}H_{23}N_3,2HCl,2H_2O$ requires N, 10·45; Cl, 17·65%). It was extremely soluble in water and alcohol. (IV) was also prepared by hydrolysing the *p*-toluenesulphonamide of 1-(β-*diethylaminoethyl*)*amino*-5 : 10-*dihydroacridine* prepared in the usual manner; m. p. 88° (Found: C, 70·0; H, 7·2. $C_{26}H_{31}O_2N_3S$ requires C, 69·6; H, 6·9%).

δ-*Chloro*-α-*diethylaminopentane.*—α-Diethylamino-δ-hydroxypentane (0·5 g.) in chloroform (1 c.c.) was added slowly to 2 c.c. of thionyl chloride in chloroform (2 c.c.). After 2 hours the chloroform and the excess of thionyl chloride were removed in a vacuum at 30°. Excess of 10% sodium hydroxide solution was added, and the base extracted immediately with ether. On removal of the ether at room temperature, the chloro-base was obtained as a yellow oil. This formed a *methiodide*, which crystallised from acetone–ether in white prisms, m. p. 116° (Found: C, 36·9; H, 7·1; N, 4·7. $C_{10}H_{23}NClI$ requires, C, 37·5; H, 7·2; N, 4·4%). The alcohol does not give a crystalline methiodide.

The chloro-base slowly isomerised to give a deliquescent solid, which gave a *picrate*, yellow needles, m. p. 270° (decomp.) (Found: C, 47·9; H, 5·9. $C_9H_{20}N,C_6H_2O_7N_3$ requires C, 48·5; H, 5·9%).

1-(p-*Nitrobenzyl*)*aminoacridine* (VI).—1-Aminoacridine (1·9 g.), *p*-nitrobenzyl bromide (2·1 g.), and sodium acetate (0·8 g.) in alcohol (30 c.c.) were heated on the water-bath for 30 hours. After cooling, the *solid* was collected, washed with water and alcohol, and crystallised from a large volume of dilute alcohol, giving dark red needles (2·6 g.), m. p. 170° (Found: C, 72·4; H, 4·8; N, 12·7. $C_{20}H_{15}O_2N_3$ requires C, 72·9; H, 4·6; N, 12·8%).

1-(p-*Aminobenzyl*)*aminoacridine.*—The nitro-compound (0·2 g.) was reduced by tin and hydrochloric acid, and the amino-compound obtained as the *dihydrochloride*, which formed purple needles, m. p. 168°, from alcohol–ether (Found: C, 61·9; H, 5·8. $C_{20}H_{17}N_3,2HCl,H_2O$ requires C, 61·5; H, 5·4%). The *dipicrate* formed red needles, m. p. 178° (decomp.), from alcohol (Found: C, 51·0; H, 3·85. $C_{20}H_{17}N_3,2C_6H_3O_7N_3$ requires C, 50·7; H, 3·4%).

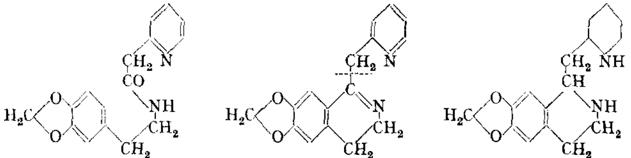
Our thanks are due to the Medical Research Council for a grant and one of us (W. H.) is indebted to Durham County Council for an Exhibition.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, March 27th,* 1936.]

137. *The Synthesis of α-Picolylisoquinolines as Possible Antimalarials. Part I.*

By G. R. Clemo, H. McIlwain, and W. McG. Morgan.

It is well known that a large number of *iso*quinoline compounds possess physiological action and that some, such as emetine, have a specific action on protozoa. In the present search for compounds of antimalarial value, it was therefore decided to prepare compounds intermediate in structure between the quinine and the *iso*quinoline alkaloids, such as (II). This compound has a part of the "second half" of the quinine molecule attached in the 1-position to the nitrogen of an *iso*quinoline nucleus, whereas in quinine it is in the 4-position to the quinoline nitrogen atom, and such compounds might be expected to exhibit interesting physiological properties even if they do not act as antimalarials.



(I.) (II.) (III.)

Pyridyl-2-acetic ester condenses readily with β-3 : 4-methylenedioxyphenylethylamine, yielding the *amide* (I), which (compare Decker, *Ber.*, 1909, **42**, 2075) undergoes ring closure with phosphorus oxychloride to 6 : *7-methylenedioxy-*1*-α-picolyl-*3 : *4-dihydro*iso*quinoline* (II). This is a yellow crystalline solid which forms a *monopicrate* and a stable water-soluble *dihydrochloride*. It is reduced smoothly to the 1 : 2 : 3 : *4-tetrahydro*-compound by means of zinc in sulphuric acid and completely to 6 : 7-methylenedioxy-1-α-pipecolyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (III) by hydrogen in the presence of platinum. These two compounds have been obtained as viscous distillable liquids, forming *dipicrates* and colourless water-soluble *dihydrochlorides*.

It has not been found possible to obtain 6 : 7-methylenedioxy-1-α-picolyl*iso*quinoline from the dihydro- or the tetrahydro-compound by the usual methods of dehydrogenation, the only isolable products being α-picoline and 6 : 7-methylenedioxy*iso*quinoline formed by the fission indicated in (II).

Experimental.

Pyridyl-2-aceto-3′ : 4′-methylenedioxy-β-phenylethylamide.—Ethyl pyridyl-2-acetate (2·5 g.) and 3 : 4-methylenedioxy-β-phenylethylamine (Haworth, Perkin, and Rankin, J., 1924, **125**, 1694) (2·5 g.) were heated under reflux at 200° for 1 hour; alcohol and a little α-picoline were evolved, leaving a brown viscous liquid, which was extracted with light petroleum. The solvent was concentrated; the *amide* then separated in colourless needles (3·5 g.), m. p. 89° (Found: C, 67·9; H, 5·8. $C_{16}H_{16}O_3N_2$ requires C, 67·6; H, 5·6%), very soluble in the commoner organic solvents except light petroleum.

6 : *7-Methylenedioxy-*1*-α-picolyl-*3 : *4-dihydro*iso*quinoline.*—The above amide (6·0 g.) was refluxed with phosphorus oxychloride (30 c.c.) for 40 minutes; the solution, originally straw-coloured, became red and was then poured gradually on ice, and the whole basified with sodium carbonate and extracted with ether. After removal of the ether the *dihydro*iso*quinoline* crystallised from alcohol in yellow needles (3·0 g.), m. p. 105° (Found: C, 72·4; H, 5·4. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3%). The compound is soluble in organic solvents but insoluble in water; its salts with the mineral acids are very soluble in water. A red compound (2·0 g.) obtained as a by-product in this reaction can be extracted with chloroform from its aqueous suspension after the ether extraction. Attempted ring closures under milder conditions (with phosphorus oxychloride or pentachloride in toluene or chloroform) did not give better results.

6 : *7-Methylenedioxy-*1*-α-picolyl-*3 : *4-dihydro*iso*quinoline dihydrochloride* was prepared by adding excess of alcoholic hydrogen chloride to an ethereal solution of the base (0·8 g.); the

bright yellow precipitate (1·0 g.), recrystallised from alcohol–ether, formed bright yellow prisms, m. p. 210° (Found: C, 56·0; H, 5·7. $C_{16}H_{14}O_2N_2,2HCl,C_2H_6O$ requires C, 56·0; H, 5·7%). The *picrate* (yellow plates, m. p. 210° after softening at 205°, from alcohol) was prepared by mixing alcoholic solutions of the base and picric acid (Found: C, 52·9; H, 3·5. $C_{16}H_{14}O_2N_2,C_6H_3O_7N_3$ requires C, 53·3; H, 3·5%).

6 : 7-*Methylenedioxy*-1-α-*picolyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*.—The above dihydro-compound (1·0 g.), zinc dust (3·0 g.), copper sulphate (0·05 g.), and water (30 c.c.) were warmed on the water-bath, and concentrated sulphuric acid (2·5 c.c.) added gradually with occasional shaking during 1 hour, so that hydrogen was only slowly evolved. The originally yellow solution became almost colourless, and was filtered, basified with sodium carbonate solution, and extracted with ether. Removal of this left the *tetrahydro*-compound as a pale yellow oil (0·8 g.), b. p. 215°/1 mm. (Found: C, 71·7; H, 6·4. $C_{16}H_{16}O_2N_2$ requires C, 71·7; H, 6·0%). The *picrate*, prepared as above, crystallised from alcohol in bright yellow prisms, m. p. 175° (Found: C, 46·1; H, 3·3. $C_{16}H_{16}O_2N_2,2C_6H_3O_7N_3$ requires C, 46·3; H, 3·1%). The *hydrochloride* was made by the addition of alcoholic hydrogen chloride to a solution of the base in alcohol; it crystallised from aqueous alcohol in fine colourless plates, m. p. 205° with softening above 200° (Found: C, 53·7; H, 5·6. $C_{16}H_{16}O_2N_2,2HCl,H_2O$ requires C, 53·4; H, 5·6%).

6 : 7-*Methylenedioxy*-1-α-*pipecolyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*.—The dihydroisoquinoline (II) as its dihydrochloride (0·25 g.), absolute alcohol (5 c.c.), and platinum oxide (0·05 g.) were shaken in hydrogen at 100 lb./sq. in. for 20 hours; the originally yellow material became white. A little water was added to dissolve the salt produced, the solution filtered from platinum, the alcohol removed, excess of sodium hydroxide solution (20%) added, and the liberated base extracted with ether. Removal of the solvent left the pipecolyl compound as an almost colourless oil (0·2 g.), b. p. 210°/1 mm. The *picrate*, prepared as above, crystallised from alcohol in fine matted needles, m. p. 236° (Found: C, 46·0; H, 4·3. $C_{16}H_{22}O_2N_2,2C_6H_3O_7N_3$ requires C, 45·9; H, 3·9%). The *hydrochloride*, prepared as was the tetrahydro-salt, crystallised from nearly absolute alcohol in colourless prisms, m. p. 293° (Found: C, 55·0; H, 7·1. $C_{16}H_{22}O_2N_2,2HCl$ requires C, 55·3; H, 6·9%).

Attempted Dehydrogenation of 6 : 7-*Methylenedioxy*-1-α-*picolyl*-3 : 4-*dihydro*iso*quinoline*.—The base (0·25 g.) and palladised charcoal (0·1 g.) were heated in an evacuated sealed tube at 200° for ½ hour. A liquid of pyridine-like odour condensed in the upper part of the tube, and yielded a picrate (0·1 g., m. p. 164° alone or mixed with α-picoline picrate). Extraction of the residue with ether yielded a solid (0·1 g., m. p. 118°) which formed a picrate, m. p. 206° (Found: C, 47·7; H, 2·9. $C_{10}H_7O_2N,C_6H_3O_7N_3$ requires C, 47·7; H, 2·5%). This analysis and the mode of production indicate that it is 6 : 7-*methylenedioxy*iso*quinoline picrate*.

Several other attempted dehydrogenations using mercuric acetate (Tafel, *Ber.*, 1892, **25**, 1622) and iodine (Buck, Haworth, and Perkin, J., 1924, **125**, 2180) failed to yield a separable product, and similar results were obtained with the 1 : 2 : 3 : 4-tetrahydro-compound.

Our thanks are due to Mr. O. Telfer for micro-analyses, and two of us (H. McI. and W. McG. M.) are indebted to the Department of Scientific and Industrial Research for maintenance grants.

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138. *Fused Carbon Rings. Part X. Some Fundamental Properties of the* 0 : 3 : 3-bicyclo*Octane Ring*.

By J. W. BARRETT and R. P. LINSTEAD.

THE experiments described in this paper bring to light a number of fundamental differences between the 0 : 3 : 3-*bicyclo*octane ring system, formed by ortho-fusion of two 5-membered rings, and the decalin system, formed similarly from two 6-membered rings. We find that (1) *trans*-0 : 3 : 3-*bicyclo*octane has a higher heat of combustion than its *cis*-isomeride, whereas in the decalin series the reverse is true. (2) Two well-known reactions of *cis*-decalin are its dehydrogenation to naphthalene and its rearrangement over aluminium chloride to the *trans*-isomeride. Neither of these reactions is paralleled in the *bicyclo*octane series.

Heats of Combustion.—In an earlier paper (J., **1935**, 436) it was shown that the heat of combustion of *trans*-β-*bicyclo*octanone, measured in the liquid state at constant volume, exceeded that of the *cis*-isomeride by 6·8 kg.-cals. (If the heats of combustion are calculated for the vapour state, by the application of Trouton's rule, the corresponding difference is 6·7 kg.-cals.) This was correlated with the deviation of the carbon valencies of the *trans*-ketone from the tetrahedral arrangement. Both the *cis*- and the *trans*-ketone have now been obtained in sufficient quantity for thorough purification and reduction by both the Clemmensen and the Kishner–Wolff method. The samples of the *cis*-hydrocarbon prepared by the two methods were almost identical in density, boiling point, refractivity, and heat of combustion. The *trans*-hydrocarbon prepared by both methods melted at − 30°, and in this case, owing to the comparative scarcity of *trans*-material, only the carefully purified product of the Clemmensen reaction was used for the determination of the heat of combustion. The fact that the *trans*-ketone was comparatively difficult to reduce by the Clemmensen method suggests that the reaction proceeds through the stage of an unsaturated compound; the entry of a double bond into the strained *trans*-ring would be less easily effected than in the case of the *cis*-compound. The thermochemical measurements were carried out by Dr. G. Becker of Braunschweig, to whom our thanks are due. The experimental results are on p. 614 and the mean derived values, calculated in the usual way, are below :

Heats of Combustion of 0 : 3 : 3-bicyclo*Octanes.*

	cals./g.	Kg.-cals./mol.			
	Liquid at const. vol.	Liquid at const. vol.	Liquid at const. press.	Vapour at const. press.	B. p.
cis- (Clemmensen)	10,879 ± 2·3 *	1197·7	1199·7	1208·3	136°
cis- (Kishner–Wolff)	10,878 ± 2 *				
trans- (Clemmensen)	10,934 ± 3·2	1203·8	1205·8	1214·3	132

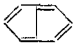
* The close agreement between these values shows that the value previously given (10,785 cals./g.; *oc. cit.*) for this hydrocarbon is erroneous, owing either to an accidental transposition of figures or to incomplete elimination of ketone during purification.

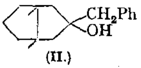
The *trans*-hydrocarbon has the higher heat of combustion by 6·0 kg.-cals. (vapour) and this confirms the result obtained with the ketones.

Hückel has calculated that the strain of the *trans*-0 : 3 : 3-*bicyclo*octane system is almost identical with that of the norcamphane (1 : 2 : 2-*bicyclo*heptane) ring. The thermochemical measurements of Becker and Roth (*Ber.*, **1934**, **67**, 627) on Alder and Stein's tetrahydrodi*cyclo*-pentadienes and -hexadienes (*Annalen*, **1932**, **496**, 197, 204, etc.) indicate that compounds containing the norcamphane ring have heats of combustion about 6 kg.-cals. above those calculated from the values for strain-free compounds of similar structure (cf. Pirsch, *Ber.*, **1934**, **67**, 1303). This is in satisfactory agreement with the difference between the *trans*- and the *cis*-0 : 3 : 3-*bicyclo*octane system.

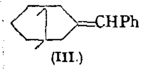
Strainless isomeric dicyclic compounds should have the same heats of combustion in the vapour state whatever the carbon skeleton. In agreement with this, Pirsch's value for 2 : 2 : 2-*bicyclo*octanone, 1104·9 (*loc. cit.*), is practically identical with our value for *cis*-0 : 3 : 3-β-*bicyclo*octanone, 1105·4 (calculated from the value for the liquid given in our previous paper, and the b. p. 195°).

Dehydrogenation.—One of the most interesting substances of the *bicyclo*octane series is the bridged *cyclo*octatetraene (I) (compare Armit and Robinson, J., **1922**, **121**, 827).


(I.)



(II.)



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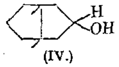


(IV.)

It would be of considerable interest to know if this hydrocarbon exhibited any aromatic properties. It has some formal resemblance to naphthalene but cannot contain an electron sextet. In view of the ease with which derivatives of naphthalene are formed by dehydrogenation, we have examined the behaviour of suitable *bicyclo*octanes both in the vapour

phase over platinum and in the liquid phase over selenium. *cis-bicyclo*Octane itself was unchanged by a platinum catalyst which dehydrogenated decalin. For work with selenium, substances of higher boiling point were necessary. *cis*-0 : 3 : 3-β-*bicyclo*Octanone was condensed with benzylmagnesium chloride to 2-*benzyl*-cis-β-0 : 3 : 3-bicyclo*octan-2-ol* (II). This was obtained in two stereoisomeric forms corresponding with the two possible positions of the benzyl group with respect to the remote *cyclo*pentane ring (compare the isomeric *cis*-β-hydrindanols of Hückel *et al.*, *Annalen*, 1926, **451**, 132; 1935, **518**, 155). When the 2-*benzylidene*-cis-0 : 3 : 3-bicyclo*octane* (III), obtained by their dehydration, was heated with selenium at 300—330°, it was partly unchanged and partly decomposed. In control experiments, 2-benzyl-*trans*-octalin was smoothly dehydrogenated at 300—330° to 2-benzylnaphthalene. Our experiments with the latter substances differ only in detail from those of Cook and Hewett (this vol., p. 62), an account of which appeared while this paper was being prepared. Although the unsaturated hydrocarbon of the decalin series presumably contains the double bond in the 6-membered ring by analogy with benzyl*cyclo*hexene (Cook and Hewett, *loc. cit.*), we think it more probable that the corresponding *bicyclo*octane derivative is the benzylidene compound (III) because of the comparative instability of the *cyclo*pentene ring. The benzyl*bicyclo*octene formula is not, of course, excluded. These results, although negative, provide some experimental support for the view that naphthalene is a unique dicyclic hydrocarbon and that the *bicyclo*octatetraene (I) does not possess aromatic characteristics.

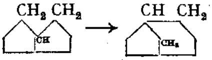
On reduction, either catalytically or by means of sodium, *cis*-β-*bicyclo*octanone yielded the corresponding *alcohol* (IV). This was obtained as a mixture of two stereoisomeric forms, corresponding to the two forms of benzyl*bicyclo*octanol. The pure isomerides were not isolated. The mixed *cis*-β-*bicyclo*octanol was mainly unchanged by selenium at 300°, yielding only a little *bicyclo*octene. *trans*-β-Decalol also appeared to be stable under these conditions.

Action of Aluminium Chloride.—Zelinski and Turowa-Pollak (*Ber.*, 1932, **65**, 1299; compare *ibid.*, 1925, **58**, 1292; 1929, **62**, 1658) have shown that *cis*-decalin is converted apparently irreversibly into the *trans*-isomeride by standing at room temperature in contact with aluminium chloride. When *cis*-0 : 3 : 3-*bicyclo*octane was similarly treated, a more fundamental change occurred. The bulk of the hydrocarbon was converted into a crystalline isomeride, m. p. 132°. This was saturated and hence dicyclic. Molecular-weight determinations showed it to be monomeric, and in agreement with this it was extremely volatile. It was clear that a rearrangement of the carbon skeleton had occurred, and from the high melting point it was probable that one or more carbon atoms were present in a bridge. A strain-free stable substance which might be formed in this way was 2 : 2 : 2-*bicyclo*octane (V), but this was excluded by its m. p. (168°; Alder and Stein, *Annalen*, 1934, **514**, 13; Komppa, *Ber.*, 1935, **68**, 1267). The bold crystalline form of our material precluded its being an impure specimen of (V) and we thought it most probable that it was 1 : 2 : 3-*bicyclo*octane (VI).

Experiments on the preparation of this hydrocarbon were undertaken, but while they were still in progress Komppa, Hirn, Rohrmann, and Beckmann (*Annalen*, 1936, **521**, 242) reported a rational synthesis of 1 : 2 : 3-*bicyclo*octane, m. p. 134°, by the method which we had contemplated and which provides a proof of the structure. Through the kindness of Professor Komppa we have examined a sample of his synthetic hydrocarbon. It is identical in all respects with our material and does not depress its melting point.*

The rearrangement of 0 : 3 : 3- into 1 : 2 : 3-*bicyclo*octane is easily visualised and involves the migration of only one hydrogen atom and one carbon-to-carbon bond.

(V.)



(VI.)

Nevertheless the change is remarkable in that it involves the formation of a strained from a strain-free system. It is therefore analogous with the rearrangement of *cis*- into *trans*-

* Professor Komppa has independently confirmed this.

hydrindane by aluminium bromide (Zelinski and Turowa-Pollak, *Ber.*, 1929, **62**, 1658) and it appears that in the presence of an aluminium halide the direction of isomeric change is not determined predominantly by questions of strain. There is, at present, no evidence that these changes are reversible and the persistence of the less stable modifications is thus easily understood.

Hydrogenation.—Willstätter and Kametaka (*Ber.*, 1908, **41**, 1480) obtained a liquid *bicyclo*octane from α-*cyclo*octadiene which resembled the 0 : 3 : 3-*bicyclo*octanes fairly closely in physical properties. This substance was formulated as a 0 : 1 : 5-, 0 : 2 : 4-, or 0 : 3 : 3-*bicyclo*octane. The bridge was reduced by hydrogen over nickel at 200° to give a mixture of hydrocarbons derived from *cyclo*octane. In view of this, the 0 : 1 : 5-structure was considered most probable.

We find that *trans*-0 : 3 : 3-*bicyclo*octane is unchanged by passage in hydrogen over platinised asbestos at 200°. There is no rearrangement to the more stable *cis*-form nor reduction of the bridge. The activity of the catalyst was checked both before and after the experiment by the conversion of benzene into *cyclo*hexane. In our experience this catalyst is more active than nickel and as it failed to reduce the *less* stable form of 0 : 3 : 3-*bicyclo*octane, it is reasonably certain that Willstätter's hydrocarbon did not contain this arrangement.

Experimental.

bicyclo*Octanes.*—15 G. of pure regenerated *cis*-β-0 : 3 : 3-*bicyclo*octanone, 200 g. of amalgamated zinc, 150 c.c. of glacial acetic acid, and 75 c.c. of hydrochloric acid were refluxed for 7 hours in an all-glass apparatus, a current of hydrogen chloride being passed through the mixture. The hydrocarbon formed was distilled in steam and extracted from the distillate with a little ether. The extract was washed with solutions of sodium bicarbonate and bisulphite (thrice), with concentrated sulphuric acid (twice), and with water. It was dried with calcium chloride, and the solvent removed under a column. The hydrocarbon was refluxed for 2 hours over sodium and distilled from fresh sodium. Yield, 10 g. (75%), b. p. 137°/765 mm. It was then redistilled and two fractions were collected arbitrarily; these had precisely the same physical properties: $d_{4°}^{18°}$ 0·8716; $n_D^{18°}$ 1·4624; $[R_L]_D$ 34·72 (calc., 34·75); b. p. 137°/765 mm., liquid at − 80°. These figures are almost identical with those reported in Part IV. The preparation of *cis-bicyclo*octane from *cis*-β-*bicyclo*octanone semicarbazone was carried out as described in our previous paper except that the hydrocarbon was also washed with concentrated sulphuric acid. The b. p., density and refractivity were identical with those previously found (*loc. cit.*).

5·5 G. of pure regenerated *trans*-β-0 : 3 : 3-*bicyclo*octanone were reduced similarly but for 12 hours and with one-third the quantities of reagents mentioned above. The purification was the same, except that the hydrocarbon extract was washed with sodium carbonate solution, concentrated sulphuric acid (twice), semicarbazide hydrochloride solution, and water. The yield of hydrocarbon was 2·16 g. (44%); 3 g. (54%) of *trans*-ketone were recovered by dilution of the sulphuric acid and extraction with ether; and 0·3 g. of *trans*-semicarbazone from the semicarbazide washing. The recovery of material was thus practically quantitative. The *trans*-hydrocarbon had $d_{4°}^{16°}$ 0·8648, $n_D^{16°}$ 1·4638, $[R_L]_D$ 35·12 (exaltation, 0·37), b. p. 134°/760 mm., m. p. (corr.) − 30°. The *trans*-hydrocarbon prepared by Kishner–Wolff reduction melts at − 29° (corr.) and not at − 36° as reported in Part IV. 3 G. of *trans*-hydrocarbon from two Clemmensen reductions were redistilled in an all-glass apparatus for the determination of the heat of combustion.

The values determined (const. vol. at *ca.* 20°) by Dr. Becker are:

cis-0 : 3 : 3-*bicyclo*Octane (Clemmensen) 10880, 10885, 10876, 10875; mean, 10879 ± 2·3 cals./g.

cis-0 : 3 : 3-*bicyclo*Octane (Kishner–Wolff) 10881, 10875, 10877; mean, 10878 ± 2 cals./g.

trans-0 : 3 : 3-*bicyclo*Octane (Clemmensen) 10941, 10927, 10936, 10930; mean, 10934 ± 3·2 cals./g.

Dehydrogenations.—A column of platinised asbestos (Zelinski and Borisoff, *Ber.*, 1924, **57**, 150) was contained in a hard-glass tube about a metre long. Dehydrogenations were carried out at 300—320° in an atmosphere of hydrogen, purified by means of acid and alkaline permanganate, silver sulphate, and potash. The substance was allowed to flow through a fine capillary into the tube and a slight suction was maintained by a siphon. The liquid products were condensed and the gas evolved was measured in a graduated reservoir. After each experiment the tube was

thoroughly swept out with a current of purified hydrogen. In this apparatus decalin (3 c.c. during 2 hours) evolved hydrogen corresponding to 75% dehydrogenation and the product (2·4 g.) yielded 2·1 g. of naphthalene. *cis*-0 : 3 : 3-*bicyclo*Octane (2 c.c.) over the same catalyst yielded no hydrogen and the recovered hydrocarbon (1·8 c.c.) was analytically pure after two distillations from sodium (Found : C, 87·1; H, 12·7. Calc. for C_8H_{14} : C, 87·2; H, 12·8%). The physical properties were almost unchanged. The catalyst was still active towards decalin after this experiment.

Selenium dehydrogenation of benzylated compounds. Experiments with derivatives of 2-benzyldecalin are described only in so far as they supplement those of Cook and Hewett (*loc. cit.*). trans-2-*Benzyl-2-decalol* was a viscous liquid, b. p. 170°/3 mm. (Found : C, 83·8; H, 10·1. $C_{17}H_{24}O$ requires C, 83·5; H, 9·9%). Potassium hydrogen sulphate, used by Cook and Hewett, gave incomplete dehydration of this alcohol; oxalic acid was preferable. 6 G. of the alcohol were heated with 20 g. of crystalline oxalic acid for 6 hours at 120°. The product was poured into water, and the hydrocarbon isolated by means of ether. Yield, 4·5 g., b. p. 140—145°/3 mm. 24 G. of the alcohol and 40 g. of anhydrous oxalic acid, treated similarly for 5 hours, yielded 19 g. of hydrocarbon, b. p. 144—146°/3 mm. Redistillation from sodium yielded *trans*-2-benzyloctalin, b. p. 145°/3 mm., which rapidly reduced permanganate and decolorised bromine in chloroform (Found : C, 89·9; H, 9·8. Calc. for $C_{17}H_{22}$: C, 90·2; H, 9·8%). 5 G. of the hydrocarbon were heated with 10 g. of selenium for 36 hours at about 320°. The residue was extracted with ether, and the extract refluxed for several hours with sodium. After removal of solvent the residue yielded 3·5 g. of 2-benzylnaphthalene, b. p. 156—166°/3—4 mm., which soon solidified. It formed prismatic needles from alcohol, m. p. 55—56° (Found : C, 93·5; H, 6·4. Calc. for $C_{17}H_{14}$: C, 93·5; H, 6·5%). The m. p. was not depressed by authentic 2-benzylnaphthalene (m. p. 56°), but was depressed to *ca.* 40° by 1-benzylnaphthalene (m. p. 59°). The picrate melted at 93—94° alone, 93° admixed with 2-benzylnaphthalene picrate, and 81° admixed with 1-benzylnaphthalene picrate (m. p. 102°). Pure 2-benzylnaphthalene, regenerated from the picrate, melted at 57°. We are indebted to Mr. K. D. Errington for the preparation of the reference samples.

15 G. of *cis*-0 : 3 : 3-β-*bicyclo*octanone were added slowly at room temperature to the Grignard reagent prepared from 15·5 g. of benzyl chloride and 2·9 g. of magnesium in 200 c.c. of dry ether. The mixture was refluxed for 8 hours and worked up in the usual way. The colourless viscous product (18·5 g.) quickly deposited a hard crystalline mass (12·4 g., m. p. 65°), which was separated from residual liquid by suction. Crystallisation from purified light petroleum (b. p. 40—50°) gave massive transparent prisms of the solid form of 2-*benzyl*-cis-0 : 3 : 3-bicyclo-*octan-2-ol* (II), m. p. 66—67° (Found : C, 83·1; H, 9·2. $C_{15}H_{20}O$ requires C, 83·1; H, 9·3%). The liquid *isomeride* deposited practically no more solid on standing (Found : C, 83·3; H, 9·4%). Both alcohols were dehydrated with crystalline oxalic acid as described above to 2-*benzylidene*-cis-0 : 3 : 3-bicyclo*octane* (III), an unpleasant-smelling liquid, unsaturated to permanganate and to bromine, b. p. 126—127°/3 mm. (Found : C, 91·2; H, 9·2. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%). Yield, 3 g. from 5 g. of solid; 2·5 g. from 4 g. of liquid alcohol.

5 G. of the hydrocarbon and 9 g. of selenium powder were heated for 2 hours at 300° and 48 hours at 310—330°. Very little hydrogen selenide was evolved; the liquid residue, isolated by means of ether, boiled between 80°/768 mm. and 138°/10 mm. (2 g.). The most definite fraction (0·6 g., b. p. 137°/10 mm.) corresponded to unchanged hydrocarbon. All the fractions reduced permanganate and none yielded a picrate.

cis-0 : 3 : 3-bicyclo*Octan-2-ol*.—A solution of 10 g. of *cis*-β-0 : 3 : 3-*bicyclo*octanone in 200 c.c. of moist ether was reduced during 6 hours by the addition of 20 g. of sodium. The main fraction of the product boiled at 104—108°/20 mm. (3·4 g.) and a considerable amount of bimolecular material was formed. A similar reduction in the presence of an excess of acetic acid gave 6 g., b. p. 103—105°/20 mm., 92—95°/15 mm. 4·6 G. of the ketone in 50 c.c. of alcohol were hydrogenated over Adams's catalyst. 1 Mol. of hydrogen was absorbed in 12 hours, after which distillation yielded 4 g. of *bicyclo*octanol, b. p. 85—86°/10 mm. No hydrocarbon was formed. The same mixture of stereoisomeric alcohols appeared to be formed by all three methods. It had a characteristic smell and failed to crystallise even at low temperatures [Found : (method 1) C, 76·2; H, 11·0; (method 2) C, 76·0; H, 10·9; (method 3) C, 76·0; H, 11·0. Calc. for $C_8H_{14}O$: C, 76·2; H, 11·1%]. In the course of attempts to separate pure stereoisomeric forms we isolated a hydrogen phthalate, m. p. 72°, crystallising in large transparent perfect rhombs, and an apparently homogeneous phenylurethane, m. p. 116°. No solid *bicyclo*octanol could be obtained by the hydrolysis of these derivatives.

The mixed alcohols (5 g.), refluxed for 2 days with selenium at 300—310°, yielded much

hydrogen selenide, 2 g. of unchanged alcohol, 0·5 g. of a hydrocarbon, b. p. 136—140°/760 mm., probably *bicyclo*octane, and a viscous residue which failed to give a picrate. *trans*-β-Decalol, m. p. 75°, gave no naphthalene or naphthol under the same conditions, nearly all being recovered unchanged.

Reaction with Aluminium Chloride.—2 G. of aluminium chloride were sublimed into a flask and covered with 5 g. of *cis*-0 : 3 : 3-*bicyclo*octane. The mixture, protected from moisture, was kept at room temperature for 48 hours. [Later experiments showed that the formation of the solid was almost complete after 2 hours' standing.] The hydrocarbon was then removed by means of a high vacuum into a tube cooled to − 70°. It solidified and remained mainly solid at room temperature. The liquid was removed by means of a "filter-stick" and distilled (mainly at 135—136°/758 mm.). The distillate partly solidified and was separated as before. After several repetitions of this process a "permanent" liquid, b. p. 135°, m. p. − 30° to − 15°, was isolated, but, owing to the small amount, we were unable to determine whether this was crude *trans*-0 : 3 : 3-*bicyclo*octane (m. p. − 29°) or unchanged *cis*-0 : 3 : 3-*bicyclo*octane contaminated with the solid hydrocarbon. The ratio of solid to liquid was about 6 : 1. The combined solid was purified by three vacuum sublimations at room temperature, which produced bold but irregular transparent crystals, m. p. 128°. This material was dissolved in alcohol, precipitated by the addition of water, collected rapidly, and immediately transferred to an all-glass apparatus consisting of four elongated bulbs, one containing phosphoric oxide, attached to a common tube. The substance was placed in the end bulb, the pressure reduced to 1 mm., and the apparatus sealed. After 24 hours' drying, the hydrocarbon was transferred to the third bulb by cooling this to − 75°, and was finally resublimed into the fourth bulb in the same way. The product was then practically pure 1 : 2 : 3-*bicyclo*octane, m. p. 131·5—132·5°. It had a peculiar odour, was very soluble in organic solvents and extremely volatile. It sublimed readily at room temperature and pressure and was best kept in a sealed tube. It was stable to bromine and permanganate, contained no chlorine, and left no ash on sudden ignition (Found: C, 86·6; H, 12·7; *M*, cryoscopic in benzene, 104, 108. Calc. for C_8H_{14}: C, 87·2; H, 12·8%; *M*, 110). Professor G. Komppa kindly sent us a generous sample of his synthetic 1 : 2 : 3-*bicyclo*octane. This was not quite pure, m. p. 126°. As it seemed probable that the impurity was the corresponding unsaturated hydrocarbon or ketone, the material was treated with dilute potassium permanganate solution (20% of that required for complete oxidation) and distilled in steam. The solid hydrocarbon was then purified by the method described above, and finally melted at 132°, unchanged by resublimation. A mixture of the two samples of 1 : 2 : 3-*bicyclo*octane melted at 132°.

Hydrogenations.—These were carried out with the same apparatus and catalyst as for the dehydrogenations over platinum. 3 C.c. of thiophen-free benzene were passed in a free stream of hydrogen during 2 hours, the catalyst being maintained at 190—210°. The product had $n_D^{23°}$ 1·447, $d_{4°}^{23°}$ 0·796, corresponding to about 75% hydrogenation. 2 G. of *trans*-*bicyclo*octane were similarly treated during 2 hours, and the product passed over the catalyst a second time. The final product (1·5 g.) was distilled from sodium and finally alone. Before treatment the hydrocarbon had $n_D^{23°}$ 1·4604, $d_{4°}^{23°}$ 0·8580; and after treatment $n_D^{22°}$ 1·4608, $d_{4°}^{22°}$ 0·8590. The catalyst was still active towards benzene after this experiment.

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139. *Fused Carbon Rings. Part XI. The Action of Aluminium Chloride on Decalin.*

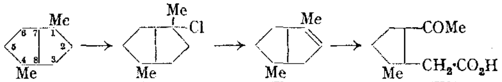
By R. L. JONES and R. P. LINSTEAD.

ZELINSKI and TUROWA-POLLAK (*Ber.*, 1925, **58**, 1292) have shown that both hydrogen iodide at 300° and aluminium bromide at 100° react with decalin with the formation of lower-boiling hydrocarbons (compare Ross and Leather, *Analyst*, 1906, **31**, 289; Baedtker and Rambeck, *Bull. Soc. chim.*, 1924, **35**, 631). Using the latter reagent, they isolated in small amount a dicyclic saturated hydrocarbon, isomeric with decalin but boiling at 160—165°, which they suggested might be a dimethyl-0 : 3 : 3-*bicyclo*octane. Although this

appeared reasonable, the evidence for it was slight and, as a general investigation of 0 : 3 : 3-*bicyclo*octanes was in progress, it was decided to reinvestigate this substance and compare its properties with those of authentic hydrocarbons of the series.

The rearrangement of decalin was conveniently effected by means of aluminium chloride at 130°. The isomerised material was accompanied by small amounts of low-boiling monocyclic hydrocarbons. Systematic fractionatiou yielded a peak fraction boiling at about 160° and resembling that obtained by Zelinski and Turowa-Pollak. This substance, which was isomeric with decalin, was unaffected by bromine, permanganate, sulphuric acid, or sulphur dioxide, and hence contained two stable rings. It was not dehydrogenated over a nickel catalyst at 300°. It is well known, particularly from Zelinski's work (*e.g.*, *Ber.*, 1911, **44**, 3124; 1912, **45**, 3678), that the capacity for dehydrogenation distinguishes *single cyclo*hexane from *cyclo*pentane rings. Two five-membered rings fused in the ortho-position, however, present a special case in which dehydrogenation is conceivable. It has now been proved experimentally that the 0 : 3 : 3-*bicyclo*octane system cannot be dehydrogenated (Barrett and Linstead, preceding paper *) and the resistance to dehydrogenation is therefore consistent with the dimethyl-0 : 3 : 3-*bicyclo*octane structure in the present instance.

Chlorination of the isomerisation product (b. p. *ca* 160°) over iodine or iron gave a mixture, from which a *monochloro*-compound, $C_{10}H_{17}Cl$, was separated. This on treatment with boiling aniline yielded an unsaturated *hydrocarbon*, $C_{10}H_{16}$. When this was oxidised by means of potassium permanganate a mixture of acids was obtained, from which a small amount of a solid *keto-acid*, $C_{10}H_{16}O_3$, was isolated. This gave iodoform on treatment with iodine and caustic soda; hence the parent hydrocarbon contained a CH_3·C⁚ group. One simple explanation for these facts is that the isomerisation product and the substances derived from it bave the formulæ (I to IV):



(I.) (II.) (III.) (IV.)

These substances are capable of existing in a number of stereoisomeric forms and the difficulty experienced in the isolation of pure compounds is easily understood.

No authentic dimethyl-0 : 3 : 3-*bicyclo*octane was available for a comparison of physical properties with those of the isomerisation product. Experiments directed towards the synthesis of the 1 : 4-dimethyl derivative (I) were unpromising and we therefore turned to the much simpler preparation of the 2 : 5-isomeride (V). This was prepared from ethyl 4-methyl*cyclo*pentanone-2-carboxylate through *4-methyl*cyclo*pentane-1 : 2-diacetic acid* by the general method previously described (Linstead and Meade, J., 1934, 935; Barrett and Linstead, J., 1935, 436).

(V.) (VI.) (VII.)

The acid was cyclised to *5-methyl*-0 : 3 : 3-bicyclo*octan-2-one* (VI), and this converted through 2 : *5-dimethyl*-0 : 3 : 3-bicyclo*octan-2-ol* into 2 : *5-dimethyl*-Δ^1-0 : 3 : 3-bicyclo*octene* (VII). No special attempt was made to separate the *cis*- and the *trans*-isomeride, but as the cyclisation to the ketone (VI) took place at about 280°, the dicyclic compounds must have been essentially *cis*-. The physical properties of the *bicyclo*octene (VII) agreed fairly closely with those of the unsaturated hydrocarbon (? III) prepared from the isomerisation product of decalin (see table). Catalytic reduction of (VII) yielded *cis*-2 : *5-dimethyl*-0 : 3 : 3-bicyclo*octane* (V). The physical properties of this are compared below with those of the isomerisation products of decalin obtained by Zelinski and Turowa-Pollak and in the present work. There is a general agreement and an indication that the material from

* Publication of the present work, which was completed in 1933, was postponed in order that this fact might be established.

decalin has the *trans*-configuration. This view would fall into line with the observation of Zelinski and Turowa-Pollak (*Ber.*, 1929, **62**, 1658) that *cis*-hydrindane is isomerised into the *trans*-modification by aluminium bromide.

Substance.	B. p.	$d_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	$[R_L]_D$.
$C_{10}H_{16}$ from decalin	160°	0·863	1·466	43·66
$C_{10}H_{16}$ synthetic	167	0·865	1·465	43·65
$C_{10}H_{18}$ from decalin (Z., T.-P.)	160—165	0·832	1·449	44·50
$C_{10}H_{18}$ from decalin (J., L.)	158—163	0·832	1·448	44·44
$C_{10}H_{18}$ synthetic	166—167	0·838	1·450	44·25

The experimental figures have been corrected to 20°, where necessary, to assist comparison.

These synthetic and analytical results therefore support, although they do not prove, the correctness of Zelinski's view of the constitution of the isomerisation product of decalin. It is reasonable to suppose that the methyl groups would be symmetrically disposed, and of the three possible positions (1 : 4-, 2 : 5-, and 7 : 8-), the 1 : 4- is the most probable from the method of formation and the 7 : 8- is excluded by the formation of the keto-acid $C_{10}H_{16}O_3$. It is curious that no solid hydrocarbons of the 1 : 2 : 3-*bicyclo*octane series (compare Part X, preceding paper) were isolated during the rearrangements. Possibly this was due to the difference in experimental conditions. The three known isomerisations of *ortho*-dicyclic hydrocarbons by aluminium chloride (*cis*- ⟶ *trans*-decalin; decalin ⟶ dimethyl-0 : 3 : 3-*bicyclo*octane; 0 : 3 : 3-*bicyclo*octane ⟶ 1 : 2 : 3-*bicyclo*octane) can all be interpreted by the breaking of *one* bond of the dicyclic structure, that connecting a bridge with an α-carbon atom, followed by the migration of one hydrogen atom and the re-formation of a carbon-to-carbon bond.

The low-boiling products of the action of aluminium chloride on decalin were fractionated and dehydrogenated. Benzene, toluene, and mesitylene were identified in the appropriate fractions, which proved the presence of *cyclo*hexane, methyl*cyclo*hexane, and 1 : 3 : 5-trimethyl*cyclo*hexane in the original material. The formation of the last must be due to drastic degradation, followed by re-synthesis. The presence of a methylhydrindane in the material boiling between 165° and 185° is probable, but no decisive evidence was obtained.

Experimental.

Isomerisation of Decalin.—Commercial decalin was dried and distilled over sodium. The product used had b. p. 185—193°, $d_{4^\circ}^{20^\circ}$ 0·8781, $n_D^{20^\circ}$ 1·4771 and hence contained about 75% of the *trans*-isomeride. Hydriodic acid at 210° for periods up to 3 days had little effect on decalin. Aluminium chloride and bromide at 100° gave some low-boiling hydrocarbons, but the reaction was very slow. Temperatures of 130—140° were the optimum, as there was a tendency for charring at 150° or higher.

A mixture of 250 g. of decalin and 80 g. of aluminium chloride was heated for 24 hours under reflux in a flask fitted with a drying tube, the temperature being maintained at 130° by means of an electrically heated oven. The hydrocarbon was decanted from the viscous lower layer of aluminium chloride complex, washed with water and alkali, dried over calcium chloride, and fractionated through a jacketed 27 cm. column of Lessing rings at the rate of 1 drop/7—8 seconds. The yield and the physical properties of the various fractions obtained by one fractionation of the product from 1 kg. of decalin, were :

Boiling range	below 150°	150—155°	155—160°	160—165°	165—170°	170—175°	175—180°
Yield, g.	15	16	31	40	45	55	31 (Total, 23%)
$d_{4^\circ}^{17^\circ}$	—	0·822	0·829	0·837	0·840	0·852	0·861
$n_D^{17^\circ}$	—	1·435	1·448	1·453	1·456	1·461	1·464

From 50—70% of decalin was recovered; this was mainly the *trans*-form and boiled at 185—186°. Further fractionation revealed a peak at about 160° and in subsequent experiments the crude product was first roughly fractionated to remove the product boiling below 180°, and this was then slowly fractionated three times. The material examined in the subsequent work, which will be referred to as fraction A, had b. p. 158—163°, $d_{4^\circ}^{20^\circ}$ 0·8320, $n_D^{20^\circ}$ 1·4482 (yield, 2—5%). In all, 8 kg. of decalin were isomerised.

In the dehydrogenation experiments the activity of nickel-alumina catalysts was found to vary considerably with the method of preparation. Zelinski's method (*Ber.*, 1924, **57**, 667) was modified as follows : Concentrated sodium hydroxide solution was added to a solution of

240 g. of nickel nitrate ($6H_2O$) and 146 g. of aluminium nitrate ($9H_2O$) until this was alkaline; a rapid stream of carbon dioxide was then passed and the precipitate was collected, and dried at 120° without washing. The dried precipitate was boiled with water, collected, and dried with alcohol and ether. The light green powder was shaken with chopped asbestos, and the mixture introduced into the silica tube of the dehydrogenator. The catalyst was reduced in purified hydrogen at 300—330°. Decalin readily yielded naphthalene when passed over this catalyst.

Fraction A (15 g.) yielded only 330 c.c. of hydrogen when circulated over this catalyst until no further gas was evolved. This corresponds to about 3% of dehydrogenation. The product was extracted thrice with liquid sulphur dioxide, in which it was almost insoluble (unlike aromatic hydrocarbons). The undissolved hydrocarbon was washed with alkali and distilled over sodium. The product had b. p. 158—163°, $d_{4°}^{20°}$ 0·8323, $n_D^{20°}$ 1·4483. It was insoluble in concentrated sulphuric acid, decolorised bromine very slowly and permanganate not at all (Found: C, 86·9; H, 13·0. $C_{10}H_{18}$ requires C, 87·0; H, 13·0%). As the physical properties were almost unaltered by this treatment, the experiments which follow were performed on fraction A without dehydrogenation.

A rapid stream of moist chlorine was passed through an ice-cooled U-tube containing fraction A and a crystal of iodine. After 5 hours the theoretical quantity for monochlorination had been absorbed; the product was dissolved in ether, washed with water and alkali, dried, and distilled. The main products were (i) recovered hydrocarbon, b. p. about 55°/15 mm., 23%; (ii) b. p. 80—90°/15 mm., 22%; (iii) b. p. 120—135°/15 mm., 5%; (iv) b. p. 135—170°/15 mm., 35%. Fractions (ii), (iii), and (iv) gave chlorine analyses corresponding approximately to those required for mono-, di- and tri-chloro-compounds. Fraction (ii) was stable in the air, but the higher fractions rapidly darkened. All had camphoraceous odours. Refractionation of (ii) gave the *monochloro*-compound (? II) in 20% yield; b. p. 88—91°/16 mm., $d_{4°}^{20°}$ 0·9823, $n_D^{20°}$ 1·4753, $[R_L]_D$ 49·2 (calc., 48·8) (Found: Cl, 20·55. $C_{10}H_{17}Cl$ requires Cl, 20·6%). The monochloro-compound was unattacked by moist silver oxide in ether. Treatment with silver *p*-nitrobenzoate yielded *p*-nitrobenzoic acid and the olefin described below. This suggests that the chlorine is tertiary.

9 G. of the monochloro-compound were boiled with 9 g. of aniline for 2 hours; charring occurred. The product was cooled in ice and the mixture of hydrocarbon and aniline was decanted from the aniline hydrochloride and distilled. The unsaturated hydrocarbon (? III), b. p. 54—60°/20 mm., was washed with dilute acid and dried over calcium chloride. Yield, 30%. It had an unpleasant odour, decolorised permanganate and bromine, and was moderately stable in the air. It had $d_{4°}^{20°}$ 0·8632, n_D^{20} 1·4663, $[R_L]_D$ 43·6 (calc. $C_{10}H_{16}|\overline{1}$ 43·6) (Found: C, 88·0; H, 11·9. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%). Quinoline, dimethylaniline, and pyridine appeared to be without action on the chloro-compound.

To 14 g. of the unsaturated hydrocarbon mechanically stirred in aqueous sodium carbonate, 2% potassium permanganate was added slowly during 8 hours until no more was absorbed. The solution was filtered from manganese mud, cleared with sulphur dioxide, acidified, and extracted with ether for 24 hours. The residue from the extract was purified with sodium bicarbonate solution in the usual way, 3·5 g. of an acid gum being obtained. This gave a dense precipitate of iodoform (m. p. and mixed m. p.) with alkali and iodine in potassium iodide. After several weeks it deposited a small quantity of diamond-shaped crystals, m. p. 120° after recrystallisation from water. This acid (Found: C, 64·9; H, 8·7. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%) (? *3-acetyl-1-methyl*cyclo*pentane-2-acetic acid*, IV) yielded iodoform and gave a semicarbazone, m. p. 195° (from acetic acid). No other solid degradation products could be isolated.

Lower-boiling fractions. The material boiling below 150°, formed by the action at 130° of aluminium chloride on 7 kg. of decalin, yielded the following fractions:

Boiling range...	to 76°	76—80°	80—90°	90—100°	100—110°	110—120°	120—130°	130—140°
$d_{4°}^{20°}$	0·737	0·757	0·761	0·766	0·771	0·768	0·770	0·781
$n_D^{20°}$	1·404	1·414	1·416	1·418	1·422	1·420	1·421	1·426
Yield, g.	14	20	17	32	17	43	21	33

These fractions were dehydrogenated by the method already described and the products were separated into aromatic and hydroaromatic portions by means of liquid sulphur dioxide. The products were redistilled, there being no substantial change in b. p. The following fractions *soluble* in sulphur dioxide were isolated:

Boiling range ...	80—90° (*a*)	90—100°	100—110° (*b*)	110—120°	120—130°	130—140° (*c*)
$d_{4°}^{20°}$	0·873	—	0·796	—	0·798	0·830
$n_D^{20°}$	1·500	1·476	1·441	1·423	1·446	1·451

The fractions *insoluble* in sulphur dioxide were very similar to the corresponding undehydrogenated material in physical properties. Fraction (*a*) was almost pure benzene from its physical properties and analysis (Found: C, 91·5; H, 8·0. Calc.: C, 92·3; H, 7·7%). It solidified in a freezing mixture. The physical properties of fraction (*b*) showed that dehydrogenation was incomplete, but nitration yielded 2 : 4-dinitrotoluene (m. p. and mixed m. p. 70°). Nitration of fraction (*c*) yielded 2 : 4 : 6-trinitromesitylene in poor yield (m. p. and mixed m. p. 231—232°). No other solid derivatives could be isolated from the dehydrogenated fractions.

Syntheses.—(a) *Attempted preparation of 1 : 4-dimethyl*bicyclo*octane (I).* α-Methyladipic ester (Dieckmann, *Annalen*, 1901, **317**, 69) was cyclised to ethyl 5-methyl*cyclo*pentanone-2-carboxylate in 70—80% yield, following the details used by Linstead and Meade (*loc. cit.*) in the case of adipic ester. The sodio-compound from 250 g. of the keto-ester, prepared in dry benzene (1 kg.) by the use of "molecular" sodium (34 g.), was treated with a slight excess of ethyl α-bromopropionate (270 g.), and the reaction completed by refluxing for 8 hours. The product, isolated in the usual way, was fractionated into *ethyl 5-methyl*cyclo*pentanone-2-carboxylate-2-α-propionate*, b. p. 171—173°/19 mm. (65%), and the corresponding open-chain ester, b. p. 180—190°/20 mm. The cyclic keto-ester had a rather garlic-like odour, gave no colour with ferric chloride, and, like other substances of similar structure, failed to condense under the usual conditions with salts of phenylhydrazine or semicarbazide (Found: C, 61·7; H, 8·1. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·1%). 100 G. were refluxed with 600 c.c. of concentrated hydrochloric acid for 24 hours, and the reagent then removed under reduced pressure. The residue on fractionation yielded 75% of *5-methyl*cyclo*pentanone-2-α-propionic acid*, b. p. 152°/6—7 mm., as a gum which solidified to small diamond-shaped crystals, m. p. 76° (from light petroleum) (Found: C, 63·3; H, 8·4. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%). The colourless phenylhydrazone melted at 192°. 70 G. of the acid were refluxed for 8 hours with 100 c.c. of ethyl alcohol, 150 c.c. of benzene, and 20 c.c. of concentrated sulphuric acid. The product was washed with water and sodium bicarbonate solution, and dried; the residue after removal of the benzene yielded 95% of the *ethyl* ester, b. p. 127—128°/12 mm., $d_{4°}^{24°}$ 1·012, $n_D^{24°}$ 1·4468 (Found: C, 66·4; H, 9·0. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·1%). This substance failed to condense with cyanoacetic ester in the presence of piperidine at atmospheric pressure (compare Barrett, Cook, and Linstead, J., 1935, 1065) and condensation by means of potassium ethoxide (Kon and Nanji, J., 1932, 2429) gave no useful product.

(b) *Preparation of 2 : 5-dimethyl*bicyclo*octane* (V). The crude β-methyladipic acid obtained by nitric acid oxidation of 500 g. of 4-methyl*cyclo*hexanol was refluxed on the steam-bath for 8 hours with a mixture of 650 c.c. of absolute alcohol, 125 c.c. of concentrated sulphuric acid, and 1½ l. of benzene. The benzene layer yielded 500 g. of β-methyladipic ester, b. p. 138—144°/16—17 mm. This was cyclised with 1¼ mols. of sodium in 2½ l. of benzene in the usual way and yielded 220 g. of ethyl 4-methyl*cyclo*pentanone-2-carboxylate, b. p. 123—125°/24 mm. (compare Dieckmann, *Annalen*, 1901, **317**, 78). Overall yield, 30% from methyl*cyclo*hexanol.

200 G. of this keto-ester were added slowly to 27 g. of "molecular" sodium in 1·5 l. of benzene. The sodio-compound formed slowly and reaction was completed by 5 hours' refluxing. 145 G. of chloroacetic ester were then added, and the mixture refluxed over-night and worked up in the usual manner, unchanged material being removed with 10% caustic potash solution. *Ethyl 4-methyl*cyclo*pentanone-2-carboxylate-2-acetate*, b. p. 180—183°/24 mm., was isolated in 65% yield. It gave no colour with ferric chloride and no semicarbazone (Found: C, 60·5; H, 7·5. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·8%). Some open-chain material was also formed.

100 G. of this ester were refluxed for 6 hours with 500 c.c. of concentrated hydrochloric acid, the mineral acid removed under reduced pressure, and the product distilled. The crude 4-methyl*cyclo*pentanone-2-acetic acid (b. p. 183—190°/24 mm.; yield, 76%) obtained was esterified after one distillation. A solution of 90 g. in 150 c.c. of ethyl alcohol was saturated with hydrogen chloride for ½ hour, kept for 4 hours, and worked up in the usual way. The neutral fraction yielded 68% of *ethyl 4-methyl*cyclo*pentanone-2-acetate*, b. p. 130—133°/23 mm., $d_{4°}^{21·5°}$ 1·0217, $n_D^{21·5°}$ 1·4439, $[R_L]_D$ 47·2 (calc., 47·6) (Found: C, 65·5; H, 8·3. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%). The semicarbazone melted at 141°.

220 C.c. of calcium-dried alcohol were treated successively with 17 g. of potassium and 49 g. of cyanoacetic ester; the whole was cooled in a freezing mixture and treated with 80 g. of the 4-methyl*cyclo*pentanoneacetic ester (compare Kon and Nanji, *loc. cit.*). The product was kept at 0° for 1 day and at room temperature for 2 days, treated with ice and dilute acid, and extracted with ether. The extract was shaken with sodium bicarbonate solution and water, and dried. The residue from the ether yielded 30 g. of *ethyl 4-methyl*cyclo*pentylidene-1-cyanoacetate-2-acetate*, b. p. 194°/4 mm., and a further quantity of this was obtained by esterifying

the acid fraction. Total yield, 35%; $d_{4^\circ}^{21^\circ}$ 1·0738, $n_D^{21^\circ}$ 1·4782 (Found: C, 65·0; H, 7·3. $C_{15}H_{21}O_4N$ requires C, 64·6; H, 7·5%). 42 G. of the ester in 100 c.c. of alcohol were reduced over 1½ g. of Adams's platinum catalyst in 24 hours. *Ethyl 4-methyl*cyclo*pentane-1-cyanoacetate-2-acetate* (92% yield) had b. p. 205°/17 mm., $d_{4^\circ}^{22^\circ}$ 1·0535, $n_D^{22^\circ}$ 1·4584, $[R_L]_D$ 72·8 (calc., 72·3) (Found: C, 63·8; H, 8·2. $C_{15}H_{23}O_4N$ requires C, 64·1; H, 8·2%).

The cyano-diester (42 g.) was refluxed with hydrochloric acid for 10 hours, and the product distilled in steam. The distillate gave a little of the semicarbazone of 5-methyl*bicyclo*octanone (compare Linstead and Meade, *loc. cit.*). The residue deposited *4-methyl*cyclo*pentane-1 : 2-diacetic acid* (38%) as crystalline flakes, very soluble in hot water, almost insoluble in cold, m. p. 173—174° (Found: C, 60·2; H, 7·95. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%). 9 G. of the di-acetic acid were heated to 270—280° with 0·9 g. of baryta. Yield of 5-methyl-0 : 3 : 3-*bicyclo*-octan-2-one (VI), 2 g. (32%). The *semicarbazone*, recrystallised from rectified spirit, had m. p. 183° (Found: C, 61·3; H, 8·8; N, 21·7. $C_{10}H_{17}ON_3$ requires C, 61·6; H, 8·7; N, 21·5%). From this the ketone was regenerated, b. p. 104°/20 mm., $d_{4^\circ}^{24^\circ}$ 0·9666, $n_D^{24^\circ}$ 1·4544, $[R_L]_D$ 39·3 (calc., 39·39).

The Grignard compound prepared from 0·4 g. of magnesium and 3 g. of methyl iodide in 20 c.c. of dry ether was treated with 1·6 g. of the ketone. After an hour, the mixture was cooled to 0° and decomposed with ice-cold dilute sulphuric acid, and the product isolated in the usual way. The alcohol was dehydrated, without purification, by slow distillation with 5% (0·05 g.) of aniline hydrobromide. 2 : 5-*Dimethyl*-Δ^1-0 : 3 : 3-bicyclo*octene* (VII) distilled at 167°; it was kept for a day over water, dried, and distilled. It had a fish-like smell and reduced permanganate. Yield, 1·0 g. (70%); $d_{4^\circ}^{24^\circ}$ 0·8605, $n_D^{24^\circ}$ 1·4649, $[R_L]_D$ 43·7 (calc. for $C_{10}H_{16}|\overline{1}$, 43·51) (Found: C, 88·0; H, 11·5. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%).

This hydrocarbon (0·8 g.) was hydrogenated over Adams's platinum catalyst (0·005 g.) without a solvent. The theoretical quantity of hydrogen was absorbed in 6 hours. The 2 : 5-*dimethyl*-0 : 3 : 3-bicyclo*octane* (V) after distillation did not attack permanganate and had a faint odour resembling that of the isomerisation product of decalin. Yield, 0·75 g.; b. p. 165—167°/760 mm., $d_{4^\circ}^{24^\circ}$ 0·8341, $n_D^{24^\circ}$ 1·4481, $[R_L]_D$ 44·25 (calc., 43·98) (Found: C, 86·8; H, 13·0. $C_{10}H_{18}$ requires C, 87·0; H, 13·0%).

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IMPERIAL COLLEGE, LONDON, S.W. [*Received, April 2nd,* 1936.]

140. *The Resolution of α-Furylmethylcarbinol.*

By D. I. DUVEEN and J. KENYON.

IN the course of investigations on the relationship between chemical constitution and optical activity, numerous secondary alcohols of the general formula CHRMe·OH have been resolved into their optically active forms. In the compounds so far examined, R has been either an open-chain, saturated or unsaturated, or a homocyclic, aromatic or hydro-aromatic, radical. With the object of extending the investigations to include alcohols in which the radical R is heterocyclic, *dl*-α-furylmethylcarbinol has been resolved into its *d*- and *l*-forms.

The following table shows that the optical rotatory dispersion of these alcohols is normal and of the same order of magnitude as that of the other secondary alcohols mentioned above.

R =	n-C_6H_{13}.	C_6H_{11}.	Ph.	CH_2Ph.	$CH_2Ph{\cdot}CH_2$.	α-C_4H_4O.
$\alpha_{4358}^{20^\circ}/\alpha_{5461}^{20^\circ}$	1·65	1·74	1·74	1·83	1·67	1·68

dl-α-Furylmethylcarbinol (Peters and Fischer, *J. Amer. Chem. Soc.*, 1930, 52, 2079) is smoothly converted into its hydrogen phthalic ester, but it is interesting to note that when the hydrolysis of the (+)- or the (−)-acid esters is effected by dilute aqueous sodium hydroxide the rotatory powers of the resulting alcohols are much reduced, whilst when aqueous sodium carbonate or steam alone is employed, the alcohol obtained is optically inactive. This type of behaviour was not noticed in the hydrolysis of the hydrogen phthalic esters

of the other alcohols enumerated above, but it occurred during the hydrolysis of (+)-γ-phenyl-α-methylallyl hydrogen phthalate (Kenyon, Partridge, and Phillips, this vol., p. 85).

A second interesting feature of (−)-α-furylmethylcarbinyl hydrogen phthalate is its interaction with cold acetic acid, by which it is converted into phthalic acid and *dl*-α-furylmethylcarbinyl acetate, whereas the hydrogen phthalic esters of purely aliphatic and of semi-aromatic (*e.g.*, phenyl-*n*-propylcarbinol) secondary alcohols are not affected by prolonged heating with glacial acetic acid.

Attempts to reduce α-furylmethylcarbinol to the corresponding tetrahydro-compound by the use of palladium and platinum catalysts under a pressure of 2 atm. were fruitless.

Specific Rotatory Powers of (−)-α-Furylmethylcarbinyl Hydrogen Phthalate in Solvents (l, 2).

Solvent.	*c.*	$[\alpha]^{19°}_{5893}$.	$[\alpha]^{19°}_{5790}$.	$[\alpha]^{19°}_{5461}$.	Solvent.	*c.*	$[\alpha]^{19°}_{5893}$.	$[\alpha]^{19°}_{5790}$.	$[\alpha]^{19°}_{5461}$.
EtOH	5·492	−3·6°	−3·4°	−3·1°	HOAc	5·050	26·9°	—	34·2°
Et_2O	4·733	9·5	10·4	11·7	$CHCl_3$	5·025	39·6	—	47·7
C_5H_5N	5·425	11·5	—	13·5	CS_2...........	5·122	68·5	75·3°	82·2

Specific Rotatory Powers of (−)-α-Furylmethylcarbinol in Solvents.

Solvent.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5790}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
EtOH	6·025	−17·0°	−18·5°	−20·4°	−33·2°
Et_2O......................................	6·100	22·6	23·6	27·0	43·2
CS_2	5·473	23·6	24·9	27·5	48·0

Experimental.

dl-α-Furylmethylcarbinol, prepared in 56% yield by addition of furfuraldehyde (0·9 mol.) to methylmagnesium bromide (1 mol.), had b. p. 162—163° and 70°/15 mm., $n_D^{15°}$ 1·4827 (Peters and Fischer, *loc. cit.*, give $n_D^{25°}$ 1·4785) (Found : C, 63·5; H, 7·0. Calc. : C, 64·2; H, 7·1%). Its p-*xenylurethane* formed white needles, m. p. 114° from benzene (Found : N, 4·5. $C_{19}H_{17}O_3N$ requires N, 4·6%). Peters and Fischer (*loc. cit.*) were unable to prepare the *acetate* by Einhorn's method : we experienced no difficulty when the reaction was allowed to proceed at room temperature, and obtained a theoretical yield, b. p. 177°/760 mm., 85°/18 mm., $n_D^{15°}$ 1·4618 (Found : C, 62·7; H, 7·0. $C_8H_{10}O_3$ requires C, 62·4; H, 6·9%).

dl-α-Furylmethylcarbinyl Hydrogen Phthalate.—Phthalic anhydride (74 g.) was dissolved in hot pyridine (45 g.), and the cooled suspension mixed with the carbinol (56 g.). The mixture was then kept at room temperature with occasional shaking for 1·5 hours. The resulting viscous liquid, dissolved in acetone (1·5 vols.), was mixed with a slight excess of dilute hydrochloric acid and ice, followed by sufficient water completely to precipitate the oily *hydrogen phthalate*, which soon set to a crystalline mass (104 g.), m. p. 77—79°. This separated from ether and light petroleum in irregular rhombs, m. p. 80° (1·124 g. required 0·179 g. NaOH. Calc. : 0·173 g.).

Resolution of the dl-*hydrogen phthalate.* Quinidine (580 g.) dissolved readily in a warm solution of the *dl*-acid ester (420 g.) in acetone (1500 c.c.) : the resulting quinidine salt (470 g., m. p. 71°), after being thrice recrystallised from acetone (1200 c.c.), formed irregular prisms (415 g.), m. p. 82°; $[\alpha]^{19°}_{5893}$ + 76·8°, $[\alpha]^{19°}_{5461}$ + 91·9°, $[\alpha]^{19°}_{4358}$ +106·2° (*c*, 5·365; *l*, 2, in chloroform). This on decomposition with dilute hydrochloric acid gave *l*-α-furylmethylcarbinyl hydrogen phthalate, which crystallised from ether and light petroleum in rosettes of cotton-wool-like needles, m. p. 61°, $[\alpha]^{19°}_{5893}$ − 39·3°, $[\alpha]^{19°}_{5461}$ − 47·6° (*l*, 2; *c*, 4·515, in chloroform).

The more soluble fractions of the quinidine salt on decomposition with hydrochloric acid yielded the *d*- + *dl*-acid ester (170 g.), which was combined with brucine (255 g.) in dry acetone (800 c.c.). After two recrystallisations from dry acetone, the brucine salt (252 g.) was obtained as a mass of hairy needles, m. p. 81°, $[\alpha]^{20°}_{5893}$ + 13·4°, $[\alpha]^{20°}_{5461}$ + 13·9° (*c*, 5·025; *l*, 2, in chloroform). On decomposition as before, this yielded *d*-α-*furylmethylcarbinyl hydrogen phthalate*, which crystallised exactly like the *l*-ester, m. p. 61°, $[\alpha]^{19°}_{5893}$ + 39·6°, $[\alpha]^{19°}_{5461}$ + 47·7° (*c*, 5·240; *l*, 2, in chloroform).

l-α-Furylmethylcarbinol, obtained by saponification of its hydrogen phthalate with aqueous 10*N*-caustic soda, had b. p. 70°/15 mm., $n_D^{15°}$ 1·4828, $\alpha^{19°}_{5893}$ − 40·07°, $\alpha^{19°}_{5790}$ − 42·0°, $\alpha^{19°}_{5461}$ −47·7°, $\alpha^{19°}_{4358}$ −81·3° (*l*, 2). This alcohol was prepared in much larger amount than was its (+)-isomeride and thus was, during its removal by distillation in steam, in contact with concentrated alkali

for a longer period. The close agreement in the magnitudes of the rotatory powers of the two alcohols suggests that but little racemisation has occurred.

The *d*-alcohol, similarly obtained, had b. p. 70°/15 mm., $n_D^{18°}$ 1·4827, $\alpha_{5893}^{18°}$ + 10·29°, $\alpha_{5790}^{18°}$ + 10·30°, $\alpha_{5461}^{18°}$ + 11·80°, $\alpha_{4358}^{18°}$ + 21·20° (*l*, 0·5). The rotatory powers of these alcohols are almost unaffected by small cbanges (*ca.* 5°) of temperature.

(—)-α-*Furylmethylcarbinyl acetate.* A mixture of the (—)-alcohol (5·6 g.), pyridine (6 g.), and acetic anhydride (6 g.) was kept at room temperature for two days and then worked up: the resulting acetate (8 c.c.) had b. p. 77°/11 mm., $n_D^{16°}$ 1·4616, $\alpha_{5893}^{16°}$ — 60·85°, $\alpha_{5790}^{16°}$ — 64·20°, $\alpha_{5461}^{16°}$ — 73·28°, $\alpha_{4358}^{16°}$ — 135° (*l*, 0·5).

Conversion of (—)-α-*Furylmethylcarbinyl Hydrogen Phthalate into the* dl-*Acetate.*—The rotatory power of the solution of (—)-α-furylmethylcarbinyl hydrogen phthalate in glacial acetic acid (see table) diminished slowly, becoming zero after 2 days; at the same time phthalic acid was deposited and the solution developed a strong odour of α-furylmethylcarbinyl acetate. In view of this result the following experiment was performed. A solution of *dl*-α-furylmethylcarbinyl hydrogen phthalate (12·5 g.) in glacial acetic acid (25 c.c.) was kept for 2 days at room temperature, then diluted with dry chloroform, and the crystals (7·3 g., m. p. 203°) removed. The filtrate yielded *dl*-α-furylmethylcarbinyl acetate (7 c.c.), b. p. 77°/11 mm., $n_D^{16°}$ 1·4617.

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141. *Optical Activity in Relation to Tautomeric Change. Part VI. Comparison of the Rates of Racemisation and of Bromination of a Ketone. A Further Study under Conditions of Basic Catalysis.*

By SHING KONG HSÜ and CHRISTOPHER L. WILSON.

IT was shown in Part IV (Ingold and Wilson, J., 1934, 773) that the speed of racemisation of an enolisable ketone in which the α-carbon atom is the centre of asymmetry is identical with its speed of bromination under equivalent conditions of acid catalysis. The example studied was 2-*o*-carboxybenzylindan-1-one. Ramberg and collaborators (*Arkiv Kemi, Min. Geol.*, 1934, **11**, *B*, Nos. 31, 41) have since examined the racemisation and bromination of α-ethylsulphonyl- and α-phenylsulphonyl-propionic acid, and Bartlett and Stauffer (*J. Amer. Chem. Soc.*, 1935, **57**, 2580) the racemisation and iodination of phenyl *sec.*-butyl ketone; in each case the rates were equal. These workers also used acid catalysts and their findings therefore simply confirm those of Part IV (*loc. cit.*).

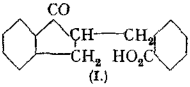
In this paper we break new ground by investigating base-catalysed reactions: the mechanism of both racemisation and halogenation must be different from those of the previous comparisons. We assume the mechanism for catalysis by a base (B) to be represented by the scheme:

$$\mathrm{CH{\cdot}C{:}O + B \rightleftharpoons [C{-\!\!-}C{-\!\!-}O]^{\ominus} + HB \rightleftharpoons C{:}C{\cdot}OH + B}$$

It is very probable that the anion is the reactive entity in unimolecular bromination and since optical activity should be lost at this stage the two rates are likely to be equal. In these circumstances each of the velocities measures the speed of formation of the anion from the ketone under the existing catalytic conditions. On the other hand it should also be pointed out that, since an enolisable ketone is a *ψ*-acid, the reversible process represented on the right of the above scheme will have a much greater velocity than that represented on the left, so that the speed of ionisation of the ketone is likely to be substantially equal to its speed of enolisation. Thus it would also be correct to say that either of the measured velocities represents enolisation.

The correspondence between the rates of racemisation and bromination was demon-

strated with *d*-2-*o*-carboxybenzylindan-1-one (I). Dilute acetic acid was the solvent, and sodium acetate (*i.e.*, acetate ions) the catalyst. Experiment showed that the speed was principally controlled by the added catalyst and not by the solvent. Both reactions were unimolecular and comparable velocity constants are 0·0438 hr.$^{-1}$ for recemisation and 0·0471 hr.$^{-1}$ for bromination. Although the difference is larger than our experimental error (less than 1%), it is possible that some systematic imperfection of method has not been eliminated.



(I.)

Experimental.

Preparation of Materials.—2-*o*-Carboxybenzylindan-1-one was prepared and resolved in the manner previously described (Ingold and Wilson, *loc. cit.*). The optically active ketone had m. p. 195—205° and $[\alpha]_D^{25°}$ + 50° (90% aqueous acetic acid, c = 1·33). Glacial acetic acid was purified by Orton and Bradfield's method (J., 1924, **125**, 960) and diluted to 16·00*N*. Crystalline sodium acetate and bromine were of AnalaR standard of purity.

Racemisation of the d-*Ketone.*—The experiments were conducted in a 2 dm. jacketed polarimeter tube maintained, by circulation of thermostat water, at a mean temperature of 25·00° ± 0·01°.

A 0·05*M*-solution of the active ketone in 16·00*N*-acetic acid containing 2·0% of crystalline sodium acetate lost activity as follows :

Time, *t* (hrs.)	0	2·42	4·70	7·42	9·7
Rotation (α)	1·45°	1·305°	1·195°	1·05°	0·95°
Time, *t* (hrs.)	22·75	25·25	29·25	33·25	46·33
Rotation (α)	0·54°	0·48°	0·40°	0·34°	0·195°

The logarithms of α when plotted against time (t) give a straight line which corresponds with a unimolecular velocity constant of 0·0438 hr.$^{-1}$

The "solvent reaction" was determined in a similar manner, the sodium acetate being omitted, but water added to the acetic acid to compensate for that present in the sodium acetate crystals used in the previous experiment. The figures were as follows :

Time, *t* (hrs.)	0	6·58	22·25	28·33	46·25	56·00	69·16
Rotation (α)	1·44°	1·38°	1·25°	1·20°	1·06°	1·00°	0·90°
Time, *t* (hrs.)	78·67	94·83	101·67	143·42	150·50	171·00	
Rotation (α)	0·84°	0·75°	0·73°	0·58°	0·55°	0·47°	

The reaction was again strictly unimolecular, the velocity constant being 0·00649 hr.$^{-1}$

Bromination.—A 0·05*M*-solution (50 c.c.) of the ketone in 16·00*N*-acetic acid in which 2·0% of crystalline sodium acetate had been dissolved was treated at 25·00° ± 0·01° with bromine, delivered from a previously calibrated capillary pipette. At determined intervals of time 5 c.c. samples of the solution were run into 50 c.c. of water in a stoppered bottle, potassium iodide added, and the iodine titrated with *N*/50-thiosulphate. Chloroform (5—6 c.c.) was added towards the end of the titration to liberate iodine adsorbed by the precipitated organic material.

Details of two experiments involving different concentrations of the halogen are in the following tables. Column 2 contains the amounts of *N*/50-thiosulphate required for a 5 c.c. sample of the reaction mixture. Column 3 gives the concentration (*M*) of brominated (x) ketone.

[Br] ~ 0·01*M*. [Ketone] = 0·05*M*.

Time, t (mins.).	Titre (c.c.).	$x(M)$ × 10^5.	Time, t (mins.).	Titre (c.c.).	$x(M)$ × 10^5.
0	4·81 *	0	115	2·63	436
15	4·56	50	135	2·28	506
35	4·15	132	155	1·96	570
55	3·70	222	175	1·67	628
75	3·35	292	195	1·38	686
95	2·98	366			

[Br] ~ 0·005*M*. [Ketone] = 0·05*M*.

Time, t (mins.).	Titre (c.c.).	$x(M)$ × 10^5.	Time, t (mins.).	Titre (c.c.).	$x(M)$ × 10^5.
0	2·72 *	0	90	1·02	340
15	2·43	58	105	0·77	390
45	1·87	170	120	0·51	442
62	1·53	238	135	0·32	480
75	1·30	284			

* Extrapolated.

A plot of log (0·05 − x) against t gives straight lines over the major portion of the reaction. Slight deviations from linearity are observable in the latter stages of halogenation, due, no doubt,

to the decrease in the concentration of the catalyst caused by the hydrogen bromide liberated. The initial slopes give first-order constants of 0·0473 hr.$^{-1}$ (for [Br] = 0·01*M*) and 0·0470 hr.$^{-1}$ (for [Br] = 0·005*M*) indicating that the reaction velocity is independent of halogen concentration.

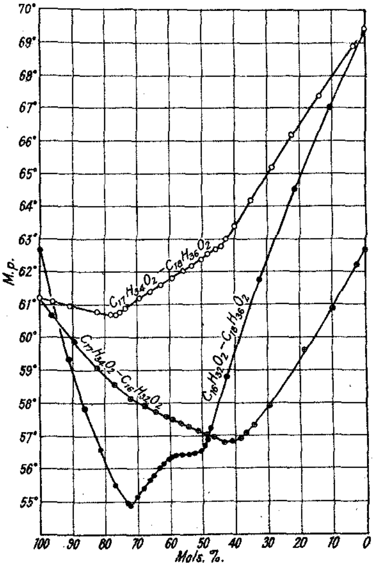
The authors are grateful to Professor C. K. Ingold, F.R.S., for his interest and help.

UNIVERSITY COLLEGE, LONDON. [*Received, March 18th, 1936.*

142. *Higher Aliphatic Compounds. Part VI. The Existence of Compounds in Binary Systems from Palmitic, Margaric, Stearic, Tricosanoic, and Tetracosanoic Acids.*

By J. C. SMITH.

SEVERAL binary systems formed by even-numbered fatty acids have been investigated, and in each case there has been evidence of a molecular compound or of a " crystal compound " involving one molecule of each acid. The clearest case is that of palmitic and stearic acids (see fig.), although de Visser (*Rec. trav. chim.*, 1898, **17**, 182) did not recognise



the significance of these results. Other examples of compound formation between " even " acids are given by Morgan and Bowen (*J. Soc. Chem. Ind.*, 1924, **43**, 346T), Bhatt and Watson (*J. Indian Inst. Sci.*, 1930, **13**, *A*, 141), and Piper, Chibnall, and Williams (*Biochem. J.*, 1934, **28**, 2182). Shriner, Fulton, and Burks (*J. Amer. Chem. Soc.*, 1933, **55**, 1494),

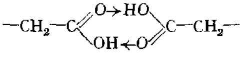
who investigated the systems of margaric acid with palmitic and with stearic acid, concluded that in " even-odd " systems no compounds were formed.

It seemed unlikely that the covalency forces would differ sufficiently to prevent compound formation between " odd " and " even " acids; nor would the dimensions of the respective crystal cells differ as much as in the pairs of " even " acids. Similarly, the m. p. of an " odd-even " compound should not be exceptionally low, and the compound should form solid solutions with each of the acids.

In the system of " odd-even " acids, tricosanoic acid–tetracosanoic acid (Chibnall, Piper, and Williams, *Biochem. J.*, 1936, **30**, 100; Ashton, Robinson, and Smith, this vol., p. 283), a curve can be drawn almost through the points to make a simple Type III system of solid solutions; but close inspection shows that the small but definite change in direction near the middle of the system is just what would occur if a compound was formed. Owing to lack of materials it was impossible to investigate the system further, and moreover, it was thought that more decisive evidence would be obtained from a study of acids of lower molecular weight.

The materials used by Shriner, Fulton, and Burks melted 1—2° below the accepted values, and these depressions may represent several units % of impurity. Actually, the effect of these impurities has been to smooth out and almost to obliterate the significant changes in the curves. In a similar way, Efremov (*Ann. Inst. Polyt. Ural*, 1927, **6**, 155), by using impure palmitic and stearic acids, completely missed the inflections characteristic of the " even-even " system. The systems formed by *pure* margaric acid show compound formation, the double molecules of palmitic acid (P_1–P_1), margaric acid (M_1–M_1), and stearic acid (S_1–S_1) giving place in mixtures to (M_1–P_1) and (M_1–S_1) " compounds." But the shape of the liquidus curves indicates that there may also be (M_3–P_1), (M_3–S_1), and (M_1–S_3) " compounds."

The view usually accepted (Sidgwick, *Ann. Reports*, 1933, **30**, 115) of the mode of association of carboxylic acids in the liquid state allows of the linking of only two molecules (see inset). A regular arrangement in the *crystal* of units of (M_1–M_1) and (M_1–S_1), perhaps alternate layers of these units, might be called for by the crystal symmetry, and the breaking up of this pattern might cause the liquidus curve to have a shape indicating apparent (M_3–S_1) units.



Experimental.

Purification of Materials.—Palmitic acid. The specimen described in Part I (J., 1931, 802) had f. p. and m. p. 62·67° ± 0·05° (m. p. in a capillary tube, 63·5°), and a new preparation gave the same values; de Visser (*loc. cit.*) gives m. p. 62·62° (cf. Francis and Collins, this vol., p. 138).

Stearic acid. Purified as in Part I, the substance had f. p. and m. p. 69·42° ± 0·05° (m. p., capillary tube, 70·5°); de Visser (*loc. cit.*) gives m. p. 69·32°.

Margaric acid. The specimen described in Part IV (J., 1933, 636) when tested with the thermometer used above had f. p. 61·17°, m. p. 61·19° ± 0·05° (m. p., capillary tube, 61·5—62°), and new specimens gave the same values. Garner and King (J., 1929, 1860) give f. p. 60·81°.

Measurement of Temperatures.—Anschütz thermometers were used to avoid correction for exposed stem. Thermometers used in this type of work need frequent standardisation, as heating above the range may cause a permanent expansion of the bulb and consequent low readings. There are also day-to-day variations of 0·01—0·02°.

Mixtures of Palmitic and Margaric Acids.—These all crystallised with very little supercooling; mixtures containing 40—70% of margaric acid gave better-defined crystals than were obtained from compositions just outside these limits. The m. p.'s (liquidus points) were taken with very slow heating of the melt, and are not more than 0·02° above the true liquidus points. Solidus points were not determined, but cooling curves for several of the mixtures showed that the whole process of solidification was completed within 0·5—1·0°. F. p.'s where determined were within 0·03° of the m. p.'s.

Mixtures of Margaric and Stearic Acids.—For mixtures containing 3—40% of margaric acid, varying m. p.'s were obtained unless the temperature of the bath was kept within 1° of that

of the melt; in the rest of the system the behaviour was normal. Cooling curves failed to show a discontinuity or second arrest such as that which indicated the non-congruent m. p. of the compound formed from hexadecyl and octadecyl iodide (Part II, J., 1932, 740).

Palmitic Acid–Stearic Acid.—The curve in the figure is drawn from de Visser's data, by conversion of weight % into molecules %.

Tetracosanoic Acid.—A re-examination of the figures previously given (this vol., p. 285) showed that for the pure acid the m. p. had not been fully corrected, and that it should be 83·87° ± 0·05° (m. p. in a capillary tube 84—84·5°). For the mixtures with tricosanoic acid the values are as recorded.

Margaric–palmitic acid mixtures.

$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.
100·0	61·19°	72·1	58·11°	56·6	57·35°	43·5	56·76°	29·45	57·89°
96·5	60·67	67·75	57·89	54·3	57·25	41·2	56·80	18·7	59·59
89·6	59·85	64·2	57·70	51·5	57·12	38·55	56·89	9·9	60·84
82·35	59·06	61·1	57·56	48·9	57·00	36·8	57·06	2·5	62·18
77·1	58·54	59·3	57·47	46·7	56·93	34·2	57·31	0·0	62·67

Margaric–stearic acid mixtures.

$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.	$C_{17}H_{34}O_2$, mols. %.	M. p.
100·0	61·19°	75·5	60·72°	59·3	61·77°	45·7	62·68°	28·5	65·16°
96·0	61·08	73·7	60·83	55·95	62·00	44·0	62·76	22·5	66·16
90·85	60·93	69·15	61·17	53·1	62·17	42·8	62·97	14·05	67·44
82·6	60·76	66·0	61·36	50·05	62·36	40·2	62·36	3·65	68·87
78·3	60·67	62·85	61·56	48·15	62·51	35·1	64·15	0·0	69·42
76·85	60·66								

The author's thanks are due to Miss P. C. Carey for the preparation of some of the margaric acid.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, March 19th,* 1936.]

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143. *Constituents of the Bark of* Zanthoxylum americanum *(Mill). Part I. Xanthoxyletin.*

By (MISS) JANET C. BELL, ALEXANDER ROBERTSON, and T. S. SUBRAMANIAM.

THE crystalline substance which, according to Gordin (*J. Amer. Chem. Soc.*, 1906, **28**, 1649), was first isolated from the bark of the prickly ash, *Zanthoxylum americanum* (Mill), by Staples and named xanthoxyline (*Amer. J. Pharm.*, 1829, **163**), has been studied by Witte (*Arch. Pharm.*, 1878, **212**, 283), Maffet (*Amer. J. Pharm.*, 1886, 672), Lloyd (*ibid.*, 1890, 229), Eberhardt (*ibid.*, 1890, 5, 230), and Gordin (*loc. cit.*). Witte, who named his material xanthoxyloin, proposed the empirical formula $C_{14}H_{14}O_4$, but Gordin, to whom we owe the first detailed examination of the compound, m. p. 132·5°, found the formula to be $C_{15}H_{14}O_4$ and suggested the name xanthoxylin N to distinguish this substance from other natural products which had been previously isolated from related genera and to which the name xanthoxylin had been applied (compare Stenhouse, *Annalen*, 1854, **89**, 251; 1857, **104**, 237; Eberhardt, *loc. cit.*; Colton, *Amer. J. Pharm.*, 1890, 191). Gordin found that the compound contained a methoxyl group, was devoid of hydroxyl or keto-groups, gave a hydrated dibromide, and yielded a dihydro-derivative on treatment with hydrogen iodide. Though unable to determine the function of the three remaining oxygen atoms, this author suggested that a lactone or acid anhydride group might be present.

In the course of an examination of the complex mixture of substances present in the bark of prickly ash we have isolated by an improved method the compound, m. p. 133°, described by Gordin (*loc. cit.*) and have confirmed the empirical formula $C_{14}H_{11}O_3(OMe)$ and general properties ascribed to it by this author. In order to avoid confusion with other well-defined compounds bearing the name xanthoxylin (compare Gordin, *loc. cit.*;

Bocquillon, *Rep. Pharm.*, 1917, **28**, 66; Dieterle and co-workers, *Arch. Pharm.*, 1931, **269**, 384) we have re-named the substance, m. p. 133°, xanthoxyletin.*

Although xanthoxyletin does not contain a phenolic hydroxyl group and is almost insoluble in water (dilution of an alcoholic solution with water precipitates the compound), it cannot be precipitated by addition of excess of water to a solution in a little alcohol containing an equivalent of sodium hydroxide. Saturation of this alkaline aqueous-alcoholic solution with carbon dioxide, however, slowly but almost completely precipitates xanthoxyletin. This property, which is shared by some coumarins, together with the fact that the usual tests indicated the presence of at least one ethylenic linkage, led us to believe that xanthoxyletin contained an α-pyrone ring system and had in all probability the skeleton C_5–(C_6·C:C·CO·O), in which, by analogy with the rotenone series, the C_5 residue was probably present as an isoprene unit. In accordance with the coumarin hypothesis it was found that xanthoxyletin is readily converted into the unsaturated monobasic acid, O-*methylxanthoxyletinic acid*, by application of Canter and Robertson's standard procedure for converting a coumarin into the O-methyl ether of the corresponding cinnamic acid. Further, hydrolytic fission with boiling 25% aqueous sodium hydroxide gives rise to acetone and a comparatively good yield of phloroglucinol monomethyl ether, which is conveniently characterised by conversion into the *di*-p-*nitrobenzoate*. The isolation of a phloroglucinol derivative in this manner clearly defines the nature of the C_6 residue.

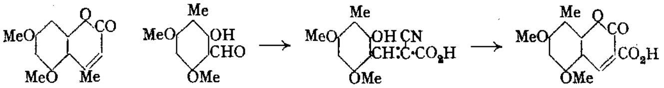
Hydrogenation of xanthoxyletin with the aid of a palladium catalyst furnished dihydroxanthoxyletin, m. p. 145—146°, which appears to be identical with Gordin's dihydro-derivative, m. p. 142—143° (*loc. cit.*), and is converted by the standard procedure into O-*methyldihydroxanthoxyletinic acid*. The latter compound is readily hydrogenated with a palladium catalyst, forming O-*methyltetrahydroxanthoxyletinic acid*, identical with a specimen prepared directly in the same manner from O-methylxanthoxyletinic acid.

Degradation of xanthoxyletin by the usual oxidising agents appears to be difficult to control. With neutral permanganate solution a complex oxidation mixture was obtained which has not yet been completely investigated, but oxidation in alkaline solution with an excess of aqueous potassium permanganate gave rise to α-hydroxy*iso*butyric acid, which in conjunction with the production of acetone by hydrolytic fission definitely establishes the presence of the group $Me_2\dot{C}$—C: in the molecule, a result in keeping with the assumption that the C_5 residue has the isoprene skeleton. Ozonolysis under strictly controlled conditions produced a mixture from which a small yield of a product $C_{10}H_5O_4(OMe)$ was readily isolated. This compound, which we have named apo*xanthoxyletin*, has the properties of an o-hydroxy-aldehyde, giving a ferric chloride reaction and forming a *phenylhydrazone* and a *triacetyl* derivative which is presumably a benzylidene diacetate. On reduction under conditions whereby phenolic aldehydes are converted into C-methyl phenols (Asahina and Tukamoto, *Ber.*, 1933, **66**, 897) *apo*xanthoxyletin yielded a phenolic compound, *deoxy*apo*xanthoxyletin*, which is easily soluble in alkalis but is devoid of aldehydic properties and does not give a ferric reaction. This phenol was readily methylated by the methyl iodide–potassium carbonate method, forming O-*methyldeoxy*apo*xanthoxyletin*, which, on the basis of the α-pyrone hypothesis (see above) together with the foregoing analytical results, was considered to be a C-methyl derivative of 5 : 7-dimethoxycoumarin (Type I, V, or VII).

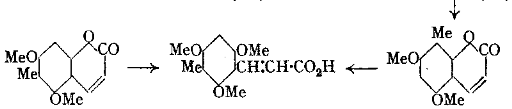
In order to test this view 5 : 7-*dimethoxy*-8-*methylcoumarin* (VII) was synthesised by the following procedure : Interaction of the aldehyde (II) and cyanoacetic acid in the presence of aqueous sodium hydroxide gave rise to the salicylidenecyanoacetic acid (III), which, on simultaneous hydrolysis and ring closure, followed by decarboxylation of the resulting coumarin-3-carboxylic acid (IV), furnished the *coumarin* (VII). Direct comparison, however, showed that the methyl ether of deoxy*apo*xanthoxyletin was not identical with the coumarin (VII) or with 5 : 7-dimethoxy-4-methylcoumarin (I) (Robertson and co-workers, J., 1931, 1255) and therefore it seemed likely that the methyl ether of deoxy*apo*xanthoxyletin had the structure (V). This was conclusively established by the fact that by the

* As we have now shown the compound to be an α-pyrone, this designation is in accordance with the names skimetin, fraxetin, etc., applied to other natural coumarins.

usual procedure the latter compound was almost quantitatively converted into 2 : 4 : 6-*trimethoxy-3-methylcinnamic acid* (VI), identical with a specimen obtained in the same

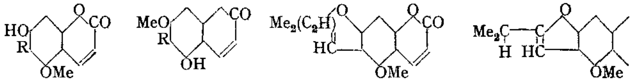


(I.) (II.) (III.) (IV.)

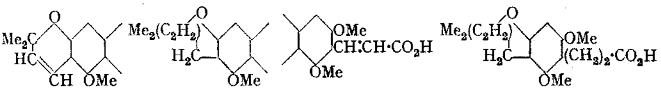


(V.) (VI.) (VII.)

manner from the synthetic coumarin (VII). It follows, therefore, that deoxy*apo*-xanthoxyletin must be either 7-hydroxy-5-methoxy- (VIII, R = Me) or 5-hydroxy-7-methoxy-6-methylcoumarin (IX, R = Me) and hence *apo*xanthoxyletin must have structure (VIII, R = CHO) or (IX, R = CHO). The evidence at our disposal does not enable us to distinguish between the two pairs of formulæ.



(VIII.) (IX.) (X.) (XI.)



(XII.) (XIII.) (XIV.) (XV.)

The formation of a tetrahydro-derivative of O-methylxanthoxyletinic acid together with the results of ozonolysis clearly shows that, in addition to the double bond in the α-pyrone ring, a second double bond must be present in the C_5 residue of xanthoxyletin. This conclusion is not invalidated by the fact that xanthoxyletin itself forms only a dihydro-compound, because under the conditions employed for hydrogenation the ethylenic linkage of an α-pyrone is not usually attacked. That the fission of the second double bond by ozone is accompanied by the loss of four carbon atoms, giving rise to a 6-formylcoumarin, affords clear proof that (a) xanthoxyletin contains a C_5 unit which is attached to the coumarin residue at the 6-position, and (b) the double bond in this unit, on the assumption that it does not migrate during ozonolysis, is in the αβ-position to the coumarin residue, *i.e.*, there is present the skeleton (A), C_3·Ċ:CH·C_6·CH:CH·CO·O·. Further, since the function of three of the four oxygen atoms in xanthoxyletin has now been clearly defined—one in a methoxyl group and two in the α-pyrone ring—and since the absence of hydroxyl or keto-groups has been confirmed (compare Gordin, *loc. cit.*), the fourth oxygen atom must form an ether system with the C_5 unit in agreement with the existence of one and not two double bonds in the C_5 unit. Moreover, when the presence of the group (C_3·Ċ:CH·) in A, the production of acetone, and the formation of α-hydroxy*iso*butyric acid by oxidation with alkaline permanganate are taken into account, it is obvious that the C_5 unit must possess an isoprene skeleton and (A) can be written $Me_2(C_2H)$:CH·C_6·CH:CH·CO·O·, *i.e.*, xanthoxyletin may be represented by a structure of the type (X). Consequently it follows that the C_5 unit must be present either as in an α-*iso*propylfurano- or in an αα-dimethyl-Δ^3-chromeno-system and hence xanthoxyletin has either formula type (XI) or (XII).

Definite experimental evidence to enable a choice to be made between the two types (XI) and (XII) is lacking. Ozonisation of (XI) would be expected to give rise to *iso*butyric acid in addition to the 6-formylcoumarin (VIII, R = CHO), but so far we have been unable to detect the former in the mixture resulting from ozonolysis. On the other hand, the production of (VIII, R = CHO) from a structure of the chromene type (XII) by means of ozone clearly involves the assumption that the degradation proceeds further than would be normally expected. Regarding the formation of acetone by the hydrolytic fission of xanthoxyletin, the remarks of Heyes and Robertson (J., 1935, 683) on the same topic in the case of the " second half " of toxicarol clearly apply here and further comment at this stage is unnecessary.

The structures (XIII), (XIV), and (XV) for dihydroxanthoxyletin, *O*-methylxanthoxyletinic acid, and *O*-methyltetrahydroxanthoxyletinic acid, respectively, follow from the partial formula (X) for xanthoxyletin.

EXPERIMENTAL.

Xanthoxyletin.—Finely powdered bark of *Zanthoxylum americanum* (Mill) (4 kg.) was extracted in a large Soxhlet apparatus with ether for 4—6 days. After evaporation of the solvent the green extract partly crystallised on being kept for 5—6 days and was then triturated with light petroleum (b. p. 40—60°) (3 l.). 3 Days later the green solid (150 g.) was collected, washed with light petroleum until the washings were colourless, and dried. From this material xanthoxyletin can be conveniently isolated by two methods.

(A) A solution of the green product (85 g.) in boiling alcohol (300 c.c.) was cooled to about 40°, gradually treated with 20% aqueous sodium hydroxide (90 c.c.), cooled, diluted with wate (approx. 2 l.), mixed with charcoal, and filtered. Carbon dioxide was passed into the filtrate fo 2 days; *crystalline material began to separate in the course of 24 hours and 3 days later the soli* was collected, well washed, and recrystallised from 80% methyl alcohol (charcoal). Pur xanthoxyletin was isolated from the resulting material by crystallisation from methyl alcoh (3—4 times) and then from ethyl alcohol (6—8 times), being finally obtained in glistening thic prisms, m. p. 133°, which had the solubilities in organic solvents and water given by Gordi (*loc. cit.*). For analysis the substance was recrystallised from light petroleum (b. p. 60—80°), i which it is sparingly soluble, forming flat prisms [Found : C, 69·9, 69·8; H, 5·5, 5·5; OM 12·7, 12·7; *M*, 267, 270. Calc. for $C_{14}H_{11}O_3(OMe)$: C, 69·8; H, 5·4; OMe, 12·0%; *M*, 258].

(B) Repeated crystallisation of the green solid first from methyl and then from ethyl alcoh with the aid of charcoal gave xanthoxyletin, m. p. 131·5—132·5°, but the process is more tedio than method (A) and the final product is apt to be slightly coloured.

The main difficulty of obtaining pure xanthoxyletin is due to the presence of another su stance having approximately the same solubilities. This compound will be the subject of future communication.

Xanthoxyletin readily decolorises bromine water and aqueous potassium permanganate a forms a non-fluorescent orange-red solution in concentrated sulphuric acid which becomes r and then dark brown on warming. It does not react with phenylhydrazine or semicarbazi acetate, does not form an *O*-acyl derivative by any of the standard methods, and is optical inactive.

Hydrolytic Fission of Xanthoxyletin.—(A) Well-powdered xanthoxyletin (3 g.) was boil with 25% aqueous sodium hydroxide (100 c.c.) for 4 hours; the solid dissolved in ½—1 hour a the resulting brownish-yellow solution gradually became dark brown. The mixture was coo to about 60°, acidified with hydrochloric acid (Congo-red), cleared with the aid of charc filtered, cooled, saturated with ammonium sulphate, and extracted 8—10 times with eth The extracts were twice washed with saturated ammonium sulphate solution, dried, a evaporated, and the resulting brown oil, which partly solidified, was treated with aqueous sodi bicarbonate to remove traces of acidic material. Phloroglucinol monomethyl ether (1·1 was isolated from the aqueous bicarbonate mixture by means of ether (8 extractions) a purified by distillation in a vacuum and then by crystallisation from benzene, forming clust of prisms, m. p. 78—79°, identified by comparison with an authentic specimen [Found : O 21·5. Calc. for $C_6H_5O_2(OMe)$: OMe, 22·1%]. A mixture of the ether (0·25 g.), *p*-nitrobenz chloride (1 g.), and pyridine (4 c.c.) was kept at 90° for ½ hour, cooled, and mixed with exces dilute hydrochloric acid. The well-washed solid was ground with aqueous sodium bicarbon to remove *p*-nitrobenzoic acid, washed, and dried. Crystallised from acetic acid and then fr

benzene–alcohol, the *di*-p-*nitrobenzoate* of phloroglucinol monomethyl ether was obtained in almost colourless needles, m. p. 199—200°, identical in every way with authentic material (Found : C, 57·8; H, 3·4; N, 6·9. $C_{21}H_{14}O_9N_2$ requires C, 57·5; H, 3·2; N, 6·4%).

An authentic specimen of the di-*p*-nitrobenzoate was prepared in good yield from synthetic phloroglucinol monomethyl ether in the same manner and formed needles, m. p. 199—200°, from acetic acid or benzene–alcohol, sparingly soluble in hot alcohol, moderately soluble in benzene, and having a negative ferric reaction (Found : C, 57·7; H, 3·2; N, 6·7%).

(B) The foregoing fission of xanthoxyletin (5 g.) with 25% aqueous sodium hydroxide (150 c.c.) was repeated and after 1 hour tbe solution was distilled with the gradual addition of water so as to keep the volume of the alkaline mixture constant. In this way 200 c.c. of distillate were collected which on treatment with 2 : 4-dinitrophenylhydrazine hydrochloride in hydrochloric acid gave a yellow precipitate (1—1·2 g.), consisting mainly of acetone-2 : 4-dinitrophenylhydrazone. After being once recrystallised from a little alcohol, this material had m. p. about 105° and under the microscope the yellow crystals of the acetone-hydrazone were seen to be contaminated with a small amount of orange-red prisms. Repeated purification from alcohol finally gave the acetone-2 : 4-dinitrophenylhydrazone in yellow flat prisms, m. p. 126—127°, undepressed by an authentic specimen (Found : C, 45·7; H, 4·5. Calc. for $C_9H_{10}O_4N_4$: C, 45·4; H, 4·2%).

Oxidation of Xanthoxyletin with Potassium Permanganate.—The powdered compound (3 g.) was refluxed (agitate) with 1% aqueous sodium hydroxide (250 c.c.) until a clear solution was obtained, which was then cooled to room temperature; acidification of a test portion with mineral acid precipitated unchanged xanthoxyletin. Potassium permanganate (15 g.), dissolved in water (350 c.c.), was then introduced in the course of 24 hours until the aqueous liquor retained a permanent permanganate colour. The mixture was cleared and neutralised with sulphur dioxide, extracted several times with ether to remove traces of neutral products, acidified with hydrochloric acid, and again extracted (8 times) with ether. Evaporation of the latter extracts, which had been washed and dried, gave a brown acidic residue, from which α-hydroxy*iso*butyric acid was isolated by means of boiling light petroleum (b. p. 60—80°). The acid separated from the concentrated solution in colourless needles, which, after having been twice crystallised from the same solvent, had m. p. 77—78°, undepressed by an authentic specimen, m. p. 78—79° (Hepworth, J., 1919, **115**, 1203) (Found : C, 46·3; H, 7·7. Calc. for $C_4H_8O_3$: C, 46·2; H, 7·7%).

O-*Methylxanthoxyletinic Acid.*—20% Aqueous sodium hydroxide (72 c.c.) was added to a warm solution of xanthoxyletin (15 g.) in methyl alcohol (150 c.c.), and the mixture warmed on the steam-bath for 5 minutes. After the addition of more aqueous sodium hydroxide (100 c.c.) methyl sulphate was gradually introduced with very vigorous agitation until the mixture was neutral. Further portions of alkali and methyl sulphate were then added alternately and after this process had been repeated 2 or 3 times the reaction mixture was basified, kept at room temperature for 1 hour, and extracted with ether. The solid left on removal of the solvent consisted of the *methyl* ester of the acid. Extraction of the aqueous liquors which had been acidified with mineral acid (Congo-red) gave a small amount of the *acid*. Generally the acid and the ester were isolated together from the reaction mixture which had been acidified with hydrochloric acid and a solution of the product was boiled with 70% alcohol (100 c.c.) containing potassium hydroxide (7 g.) for 1 hour, cooled, diluted with water (100 c.c.), and acidified with excess of hydrochloric acid. 24 Hours later the precipitated *O*-methylxanthoxyletinic acid was collected, purified from traces of non-acidic material by means of aqueous sodium carbonate, dried, and crystallised from methyl alcohol and then from benzene or benzene–light petroleum (b. p. 60—80°), forming colourless prisms (13 g.), m. p. 179·5—180·5° with sintering at 178° [Found : C, 66·2; H, 6·2; OMe, 20·8. $C_{14}H_{16}O_3(OMe)_2$ requires C, 66·2; H, 6·2; OMe, 21·4%]. The compound is considerably less soluble in organic solvents, except alcohol, than xanthoxyletin. It does not give a ferric reaction and dissolves remarkably slowly in aqueous sodium bicarbonate.

The methyl ester separated from light petroleum in colourless, thick, short prisms, m. p. 78·5—79·5° (Found : C, 67·2; H, 6·5. $C_{17}H_{20}O_5$ requires C, 67·1; H, 6·6%).

Dihydroxanthoxyletin.—Hydrogen (approx. 1 mol.) was rapidly absorbed at atmospheric pressure by xanthoxyletin (2 g.), dissolved in acetic acid (50 c.c.) containing 1% palladium chloride solution (10 c.c.). Evaporation of the filtered liquid in a vacuum left an almost pure *product*, which formed colourless rhombic prisms (1·9 g.), m. p. 144·5—145·5°, from benzene and then from benzene–light petroleum (b. p. 80—100°), considerably more soluble in organic solvents than xanthoxyletin [Found : C, 69·3; H, 6·2; OMe, 11·8; *M*, 233. $C_{14}H_{13}O_3(OMe)$ requires C, 69·2; H, 6·2; OMe, 11·9%; *M*, 260]. The same compound was obtained by hydro-

genation of xanthoxyletin (1 g.) in alcohol (150 c.c.) with a palladium catalyst (from 0·1 g. of palladium chloride).

O-Methyltetrahydroxanthoxyletinic Acid.—Reduction of *O*-methylxanthoxyletinic acid (1 g.) in acetic acid (50 c.c.) with hydrogen (approx. 2 mols. absorbed) and a palladium–charcoal catalyst (from 1 g. of activated charcoal and 0·05 g. of palladium chloride) was complete in about 10 minutes. Evaporation of the filtered solution in a vacuum left the *tetrahydro-acid*, which separated from benzene and then light petroleum (b. p. 80—100°) in colourless prisms (0·95 g.), m. p. 150·5—151·5° [Found : C, 65·3; H, 7·5; OMe, 22·9. $C_{14}H_{16}O_3(OMe)_2$ requires C, 65·3; H, 7·5; OMe, 21·1%].

When the hydrogenation was carried out in alcohol containing palladium chloride, the product consisted mainly of the ethyl ester, which on hydrolysis with 5% alcoholic sodium hydroxide for 1½ hours gave the tetrahydro-acid, forming colourless needles, m. p. and mixed m. p. 150—151°, from 50% alcohol.

O-Methyldihydroxanthoxyletinic acid was prepared from dihydroxanthoxyletin (1 g.) by the procedure used for the preparation of xanthoxyletinic acid and the product was hydrolysed by being boiled with 7% alcoholic potassium hydroxide for 1 hour. The resulting acid separated from benzene in small prisms, m. p. 171—172° (Found : C, 65·9; H, 7·0. $C_{16}H_{20}O_5$ requires C, 65·8; H, 6·9%). Mixed with the tetrahydro-acid, it melted at 135—140°.

Hydrogenation of the dihydro-acid (1 g.) in acetic acid (50 c.c.) with hydrogen and a palladium–charcoal catalyst gave rise to *O*-methyltetrahydroxanthoxyletinic acid, forming colourless prisms, m. p. 150·5—151·5°, from warm light petroleum (b. p. 80—100°), identical with a specimen prepared from *O*-methylxanthoxyletinic acid.

apo*Xanthoxyletin*.—A stream of ozone and oxygen was led into a solution of xanthoxyletin (1 g.) in chloroform (150 c.c.) until the yellow colour, which the solution gradually assumed, appeared to have maximum intensity (¾—1 hour). The residue left on evaporation of the solvent was digested with water (50 c.c.) at room temperature for 12 hours and then on the water-bath for 10 minutes. On cooling, a solution of the solid product in hot alcohol deposited apo*xanthoxyletin* (0·12—0·15 g.), which, after recrystallisation from the same solvent, was obtained in colourless slender needles, m. p. 217—218° [Found : C, 59·9; H, 3·8; OMe, 14·1. $C_{10}H_5O_4(OMe)$ requires C, 60·0; H, 3·6; OMe, 14·1%]. Concentration of the alcoholic mother-liquors from the crude product gave unchanged xanthoxyletin.

Treatment with ozone for shorter periods gave comparatively little *apo*xanthoxyletin with much unchanged material, and prolonged treatment resulted in mixtures from which little or nc crystalline material could be isolated.

*apo*Xanthoxyletin is sparingly soluble in cold alcohol, acetic acid, or benzene, moderatel} easily soluble in hot alcohol, aud insoluble in light petroleum or aqueous sodium bicarbonate With aqueous sodium hydroxide the compound forms a yellow solution, from which it is pre cipitated unchanged. It gives a deep port-wine coloration with alcoholic ferric chloride and a silver mirror with ammoniacal silver nitrate at 55—60°, reduces Fehling's solution, and give (slowly) a faint coloration with Schiff's reagent and a yellow solution in concentrated sulphuri acid which is unchanged on warming.

A solution of *apo*xanthoxyletin and excess of phenylhydrazine in acetic acid was gentl warmed for several hours; the *phenylhydrazone*, which had gradually separated, was collecte 24 hours later and recrystallised from alcohol, forming slender needles, m. p. 251° (decomp (Found : C, 65·7; H, 4·5; N, 9·4. $C_{17}H_{14}O_4N_2$ requires C, 65·8; H, 4·5; N, 9·0%).

Acetylation of *apo*xanthoxyletin (0·1 g.) with acetic anhydride (2 c.c.) and pyridine (1 c.c on the water-bath for 2½ hours and then under reflux for ½ hour gave rise to the *triacetyl* deri ative, which formed colourless prisms, m. p. 151—152°, from alcohol, having a negative ferr reaction [Found : C, 56·2; H, 4·5; OMe, 8·3. $C_{16}H_{13}O_8(OMe)$ requires C, 56·0; H, 4·4; OM 8·5%]. Acetylation under less drastic conditions gave unchanged material or a mixture.

*Deoxy*apo*xanthoxyletin*.—The foregoing aldehydo-compound (0·3 g.) was reduced in acet acid (50 c.c.) with hydrogen and a palladium–charcoal catalyst (from 0·05 g. of palladium chlo ide and 1 g. of activated charcoal); the absorption (approx. 2 mols.) was complete in about minutes. After having been diluted with water (500 c.c.), the filtered solution was neutralis with sodium bicarbonate, and the *product* isolated with ether (8 extractions) and crystallis from benzene, forming slender needles (0·2 g.), m. p. 197—198°, readily soluble in alcohol ar having a negative ferric reaction (Found : C, 64·2; H, 5·2. $C_{11}H_{10}O_4$ requires C, 64·1; 4·9%). This compound gives a yellow solution with aqueous sodium hydroxide and does n exhibit reducing properties. A solution of the substance in aqueous alcohol has a bl fluorescence.

The *methyl* ether of deoxy*apo*xanthoxyletin (V) was prepared by methylation of the aforementioned substance (0·7 g.) with methyl iodide (6 c.c.) and excess of potassium carbonate in boiling acetone during 1½ hours. After the addition of more acetone (75 c.c.) the solution was filtered, acidified with acetic acid (0·5 c.c.), and evaporated, and the residual *methyl* ether was well washed with water to remove traces of potassium salts, dried, and crystallised from benzene–light petroleum (b. p. 60—80°), forming colourless slender needles (0·52 g.), m. p. 138—139°, readily soluble in hot benzene or alcohol and insoluble in aqueous sodium hydroxide [Found : C, 65·5; H, 5·5; OMe, 27·7. $C_{10}H_6O_2(OMe)_2$ requires C, 65·5; H, 5·5; OMe, 28·2%]. An aqueous-alcoholic solution of the compound exhibited a blue fluorescence.

2 : 4 : 6-*Trimethoxy-3-methylcinnamic Acid* (VI).—By means of methyl sulphate and 20% aqueous sodium hydroxide according to the standard procedure the foregoing methyl ether was converted into the *cinnamic acid* (only traces of the ester were formed during alkylation), which was purified by the aid of 1% aqueous sodium hydroxide and then by crystallisation from benzene, forming colourless prisms, m. p. 163—164°, readily soluble in alcohol or acetic acid and reacting very slowly with aqueous sodium bicarbonate [Found : C, 62·0; H, 6·4; OMe, 36·3. $C_{10}H_7O_2(OMe)_3$ requires C, 61·9; H, 6·4; OMe, 36·9%].

Reduction of this acid (0·2 g.) with hydrogen (1 mol. absorbed) and a palladium catalyst proceeded rapidly in acetic acid (20 c.c.) and gave rise to 2 : 4 : *6-trimethoxy-3-methyldihydrocinnamic acid*, which formed colourless prisms (0·15 g.), m. p. 139—140°, from benzene (Found : C, 61·1; H, 7·2. $C_{13}H_{18}O_5$ requires C, 61·4; H, 7·1%).

5 : 7-*Dimethoxy-8-methylcoumarin* (VII).—A mixture of 2-hydroxy-4 : 6-dimethoxy-3-methylbenzaldehyde (Curd and Robertson, J., 1933, 442) (1·5 g.), cyanoacetic acid (8 c.c. of a solution prepared according to the directions of Phelps and Tillotson, *Amer. J. Sci.*, 1908, **26**, 267), and 20% aqueous sodium hydroxide (5 c.c.) was agitated for 4 hours, diluted with water (100 c.c.), and acidified (Congo-red) with 8% hydrochloric acid. The yellow precipitate of 4 : 6-dimethoxy-3-methylsalicylidenecyanoacetic acid (III) (1·5 g.), m. p. 221—222° (decomp.), was converted into 5 : 7-dimethoxy-8-methylcoumarin-3-carboxylic acid (IV) (1·4 g.), m. p. 244—245° (decomp.), by being boiled with 4% hydrochloric acid (100 c.c.) for ½ hour. Decarboxylation of the latter compound (1·4 g.) was effected by boiling with quinoline (80 c.c.) and Kahlbaum's "Natur Kupfer" (5 g.) for 40 minutes. After cooling, ether (2 l.) was added and the filtered mixture was washed with 8% hydrochloric acid until all the quinoline was removed, then with aqueous sodium bicarbonate, and finally with water. Evaporation of the dried ethereal solution gave the *coumarin*, which separated from dilute alcohol in slender needles, m. p. 187—188°, readily soluble in alcohol or acetic acid and sparingly soluble in ether [Found : C, 65·4; H, 5·4; OMe, 27·6. $C_{10}H_6O_2(OMe)_2$ requires C, 65·5; H, 5·5; OMe, 28·2%]. A solution of this compound in aqueous alcohol exhibited a blue fluorescence. Mixed with the methyl ether of deoxy*apo*xanthoxyletin, it had m. p. 125—130°.

Hydrolysis of this coumarin (0·7 g.) and simultaneous methylation of the resulting acid by the standard method gave rise to 2 : 4 : 6-trimethoxy-3-methylcinnamic acid, m. p. 162—163° after crystallisation from benzene–light petroleum (Found : C, 61·8; H, 6·3; OMe, 36·4%). This compound was identical in every way with a specimen obtained from the methyl ether of deoxy*apo*xanthoxyletin. On reduction with hydrogen and a palladium catalyst it formed 2 : 4 : 6-trimethoxy-3-methyldihydrocinnamic acid, m. p. and mixed m. p. 139—140° after purification.

UNIVERSITY OF LIVERPOOL. [*Received, March 19th*, 1936.]

144. *Oxidation of Acetaldehyde and Benzaldehyde by Hydrogen Peroxide in Presence of Selenium Oxychloride.*

By J. B. FIRTH and H. H. GETHING.

THE oxidation of acetaldehyde and benzaldehyde to the corresponding acid by hydrogen peroxide takes place comparatively slowly under ordinary conditions. The addition of a little selenium oxychloride to the mixture substantially accelerates the reaction.

The rate of oxidation increases with rise of temperature. Hydrochloric acid would result from this decomposition of the selenium oxychloride, but experiments with this acid added instead of selenium oxychloride show that it does not itself materially catalyse the reaction.

With 0·5 g. of acetaldehyde, the maximum result is obtained with 0·1—0·2 c.c. of selenium oxychloride; the addition of a greater amount does not appear to affect the extent of oxidation of the aldehyde.

Experimental.

The amounts of acetic and benzoic acid produced were determined by direct titration with standard sodium hydroxide solution, phenolphthalein being used as indicator. Correction factors for the initial acidity of the aldehydes, of hydrogen peroxide, and of the products of hydrolysis of the selenium oxychloride were determined in each case. The conversion into acetic acid and benzoic acid was confirmed, and the latter acid crystallised out in the reaction vessel in the long-period experiments.

In all cases a parallel blank control was simultaneously carried out.

Typical results are given in the following tables, the results in columns 2 and 3 being the data after correction as indicated above.

Series I. Oxidation of Acetaldehyde.

0·5 G. of acetaldehyde, 25 c.c. of 20-vol. hydrogen peroxide, one drop of selenium oxychloride.

(i) Room temp., *ca.* 16°.			(ii) Temp. 20°.			(iii) Temp. 100°.			(iv) Temp. 5—6°.		
	Conversion, %.			Conversion, %.			Conversion, %.			Conversion, %.	
Time, days.	Con-trol.	Actual.	Time, days.	Con-trol.	Actual.	Time, hours.	Con-trol.	Actual.	Time, days.	Con-trol.	Actual.
2	1·3	6·2	42	11·0	77·0	1	12	71·0	50	4	23·0
6	1·5	15·0	50	12·0	80·0	2	19·5	79·5	100	5	41·0
12	3·5	26·0	63	18·5	88·5	3	28	86·0			
20	4·0	41·0									
35	7·0	56·0				H_2O_2 added in two equal proportions, the second being added after 1 hr.:					
56	11·5	64·0									
77	15·0	80·0				2	20·0	86·5			

Effect of varying the amount of selenium oxychloride added.

Duration of experiment, 15 days.

Selenium oxychloride, c.c.	0	0·05	0·1	0·2	0·3	0·5
Conversion, %	3·5	51·0	72·0	82·0	81·5	81·0

Effect of hydrochloric acid.

No selenium oxychloride. Duration of experiment, 15 days.

N/2-Hydrochloric acid, c.c.	0	0·5	0·7	1·25	1·5	2·0	5·0
Conversion, %	3·5	4·25	5·0	5·25	5·8	6·1	8·0

If 100-vol. hydrogen peroxide is used, after a slight lag, during which the mixture becomes warm, a very vigorous reaction sets in, and the mixture boils. The reaction may be kept under control by immersion in ice-water.

0·5 G. of acetaldehyde was added to 5 c.c. of 100-vol. hydrogen peroxide, then one drop of selenium oxychloride; the temperature of the mixture was kept between 5° and 7°.

Time, days	1	7	11	15
Conversion, %, in control	2	3	3	4
Conversion, %	7	16	32	35

Series II. Oxidation of Benzaldehyde.

Two sets of experiments were carried out, one at room temperature (about 16°) and the other at about 5°, the reaction vessel being shaken at intervals.

0·5 G. of benzaldehyde, 10 c.c. of 20-vol. hydrogen peroxide, and one drop of selenium oxychloride.

Room temp.			Temp. 5°.		
	Conversion, %.			Conversion, %.	
Time, days.	Control.	Actual.	Time, days.	Control.	Actual.
2	7·0	25·5	3	4·5	17·0
5	9·0	43·5	6	6·0	25·5
7	10·5	73·0	10	6·5	38·5
10	12·5	88·0	18	7·5	54·5

University College, Nottingham. [*Received, March 13th, 1936.*]

145. *The Energetics of Catalysis. Part VI. The Kinetics of Hydrogenation Processes in Liquid Systems.*

By Edward B. Maxted and Charles H. Moon.

In the preceding paper of this series (J., 1935, 1190), the modification of the Arrhenius equation, in heterogeneous processes involving adsorption catalysis, by the insertion of appropriate heats of adsorption has been discussed with special reference to the occurrence of velocity maxima in the hydrogenation of typical ethylenic compounds at a platinum surface.

According to the views of zur Strassen (*Z. physikal. Chem.*, 1934, *A*, **169**, 81) and of Schwab (*ibid.*, **171**, 421), the reversal in the sign of the temperature coefficient in the hydrogenation of gaseous ethylene is regarded as being due to the falling—as the temperature range corresponding with reversal is reached—of the adsorbed concentration of ethylene to a value which is insufficient to render the progress of the reaction independent of the change of adsorbed concentration of this gas. If, for instance in the catalytic hydrogenation of an ethylenic compound in a liquid system, the adsorbed concentration both of hydrogen and of the unsaturated substance is maintained throughout the reaction substantially above a critical concentration dependent on the rate of reaction, the kinetics of the process should be of zero order. If, on the other hand, the adsorbed concentration of either component sinks until a stage is reached at which the rate of available supply of this component, in addition to energetic factors, exerts an effective influence on the reaction rate, this zero order should no longer be followed. In practice, in the hydrogenation of ethylenic compounds in liquid systems, the supply of hydrogen is maintained at an approximately constant value throughout; and the normal kinetics are approximately of zero order (Armstrong and Hilditch, *Proc. Roy. Soc.*, 1919, *A*, **96**, 137; 1920, *A*, **98**, 27; 1921, *A*, **99**, 490; Maxted, J., 1921, **119**, 225), save towards the end of the reaction, where the residual concentration of the unsaturated compound is insufficient to preserve linearity.

It should be noted that other factors, in addition or as an alternative to those suggested by zur Strassen and Schwab, may conceivably give rise to a negative temperature coefficient. Some of these have recently been considered by Tucholski and Rideal (J., 1935, 1701) on the basis of the relative rates of hydrogenation of ethylene by hydrogen and by deuterium. There is, in such systems, the additional complication of deuterium–hydrogen substitution in the ethylene in addition to catalytic saturation; and the relative degree of effective incidence of the various suggested factors is difficult to apportion. However, if zur Strassen's conception of the factors underlying reversal is correct, the change in sign of the temperature coefficient should be accompanied by a corresponding change in the kinetic form of the reaction, which should deviate from its normal zero-order form at temperatures above the reversal point. This has now been investigated and found to deviate in the expected manner.

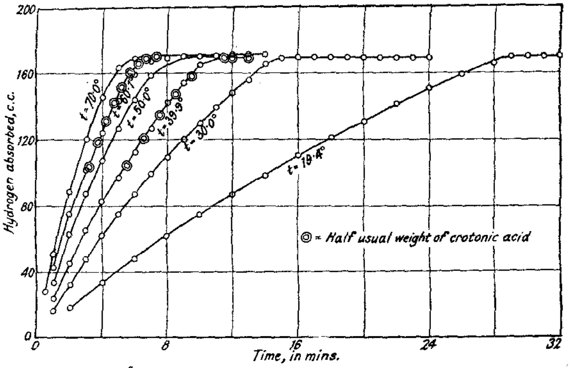
Experimental.

As a suitable ethylenic compound which could be obtained in a high degree of purity, free, above all, from traces of inhibitants and of tarry or clogging poisons, crotonic acid was taken. This was purified by repeated sublimation at a relatively low temperature ($< 100°$) and by treatment with a large excess of platinum-black, in order to remove, by adsorption, any traces of poison which might be present, the treatment being continued to a stage well beyond that at which further purification affected the hydrogenation velocity; and all supplies throughout the work were taken from the same standard purified stock. The standard platinum catalyst used, and the hydrogenation procedure and apparatus, were as already described in previous papers of the present series. Each charge consisted of the stated weight of crotonic acid, dissolved in 10 c.c. of pure acetic acid, together with 0·05 g. of platinum-black.

The general form of the reaction path at temperatures below the reversal point is shown in Fig. 1. The form is, as has also been found by other workers, approximately linear, the degree of curvature being only slight; and all the graphs show the relatively sudden and complete cessation of reaction which is characteristic of processes of zero order. The weight of crotonic acid hydrogenated was, in each case, 0·5906 g.

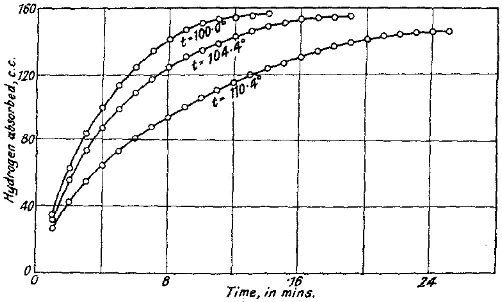
At temperatures above the reversal point (see Fig. 2), the kinetic form of the reaction apparently undergoes a fundamental change. Following a transition type during the temperature range corresponding with reversal (80—90°), the reaction path becomes evenly curved, loses its characteristic phase of sudden cessation, and, at these higher temperatures, approximates

FIG. 1.



to that of a reaction of the first order. The degree of conformity to a unimolecular path is shown in the following table, in which x is the volume, in c.c., of hydrogen absorbed after minutes; 0·574 g. of crotonic acid, corresponding with a maximum absorption of about 160 c.c

FIG. 2.



of hydrogen at 20°, was taken for each experiment of this series, in the form of a stock solution in acetic acid.

Temp. 100°.			Temp. 104·4°.			Temp. 110·4°.		
t (mins.).	x.	k.	t (mins.).	x.	k.	t (mins.).	x.	k.
2	62·4	0·107	4	87·2	0·086	8	94·4	0·048
4	100·1	0·107	6	109·1	0·083	12	115·6	0·046
6	124·9	0·109	8	125·1	0·083	16	131·0	0·046

The effect of an increase in temperature beyond the reversal point has thus involved an increasing degree of incidence of a factor which, when dominant, brings about a change in the reaction order. It is possible, moreover, that this factor may be effectively present to a subordinate degree even below the temperature range corresponding with a change in sign of the temperature coefficient, and that its presence may explain the small deviation from a linear path found at these lower temperatures, at which the order of the reaction is approximately zero.

In order to test whether the slight departure from linearity was due to a gradual, if small, diminution in the activity of the platinum, which might conceivably be caused—in spite of the preliminary purification of the crotonic acid—by the deposition on the catalytic surface of small traces of tarry or other clogging poisons, such as might be formed in small quantities as secondary products, a series of measurements was next carried out with half the above quantity of crotonic acid (0·2953 g.), together with 0·05 g. of platinum as before. The reaction was in this way begun at a stage corresponding—in comparison with the previous measurements—with that at which half of the former quantity of crotonic acid had been hydrogenated, save that the catalyst was in its initial state. Thus, if no appreciable diminution in the activity of the catalyst occurs, the reaction curves during this later series should coincide with the latter half of the former curves obtained with the full amount of crotonic acid. On the other hand, if any appreciable diminution in catalytic activity had occurred (*i.e.*, if the slight curvature were due to this factor), the employment of conditions which are equivalent to the use of fresh catalyst at the stage corresponding with semi-hydrogenation should result in a more rapid rate of reaction. The alternative method of investigation, entailing the repeated use of the same catalyst for successive hydrogenations, was impracticable owing to the small quantities involved and to the danger of activity changes during the process of recovery and re-preparation for use.

The almost complete correspondence of these later measurements with the latter half of the former runs may be seen on reference to Fig. 1, in which the relative rates of absorption have been indicated. The kinetics observed are thus those of the process in the presence of a catalyst of constant activity.

Finally, while the observed change of reaction order is in conformity with zur Strassen and Schwab's conception of the causes underlying reversal, further work in confirmation of this important quantitative introduction of the heat of association into the Arrhenius equation is undoubtedly required.

University of Bristol. [*Received, March 23rd, 1936.*]

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146. *Some Esters of Titanium.*

By J. S. Jennings, W. Wardlaw, and W. J. R. Way.

The esters of orthosilicic acid are well known, tetraethoxysilicon, $Si(OEt)_4$, having many interesting technical applications. The corresponding titanium compounds are, however, much less familiar, and in the literature many conflicting statements are recorded.

An early investigator, Demarçay (*Compt. rend.*, 1875, **80**, 51), described $Ti(OEt)_4$ as a white crystalline compound, but his analytical data were unsatisfactory. He attributed the discrepancies in his results to the presence of variable quantities of titanic acid in his product. More recent workers, Bischoff and Adkins (*J. Amer. Chem. Soc.*, 1924, **46**, 256), concluded that, although the methyl derivative $Ti(OMe)_4$ was a solid, yet the ethyl analogue was a colourless liquid, as were also the propyl and the butyl derivative. They concluded that Demarçay's compound was an oxytitanate, and that he had never isolated the ester $Ti(OEt)_4$. We have prepared this ester and find it is a liquid, thereby confirming Bischoff and Adkins's statement. Furthermore, we have reinvestigated the preparation of tetramethoxytitanium and isolated it as a white solid.

The method of preparation of the esters $M(OEt)_4$, where M = Si or Ti, emphasises a striking difference between the reactions of the tetrachlorides of these two elements. Although tetraethoxysilicon is readily obtained from the tetrachloride and alcohol, $SiCl_4 + 4EtOH = Si(OEt)_4 + 4HCl$, yet for tetraethoxytitanium the use of sodium ethoxide is necessary, $TiCl_4 + 4NaOEt = Ti(OEt)_4 + 4NaCl$.

If ethyl alcohol is used instead of sodium ethoxide, a white crystalline compound is isolated to which Demarçay assigned the formula (I) $TiCl(OEt)_3,HCl$. Prolonged action of boiling alcohol fails to alter the composition of this substance, and no hydrogen chloride is eliminated when it is confined in a vacuum over solid potassium hydroxide. This is very remarkable, for one would not have expected a molecule of hydrogen chloride to be bound so firmly to the complex. Reference to Demarçay's paper shows that his structure is based solely on the results of an analysis. Therefore, the possibility is not excluded that the compound is really (II) $TiCl_2(OEt)_2,EtOH$; in fact, his experimental data support this formula, for they explain why boiling alcohol does not eliminate hydrogen chloride.

To test the possibility that the compound had formula (II), we prepared *triethoxychlorotitanium* from the reaction between tetraethoxytitanium (1 mol.) and acetyl chloride (1 mol.): $Ti(OEt)_4 + CH_3{\cdot}COCl = TiCl(OEt)_3 + CH_3{\cdot}CO_2Et$. This compound did not combine with hydrogen chloride on being dissolved in alcoholic hydrogen chloride, but yielded instead crystals of a new *substance* $TiCl(OEt)_3,EtOH$. Crystals of the same composition were obtained by dissolving $TiCl(OEt)_3$ in a small quantity of ethyl alcohol. It seems most unlikely, therefore, that Demarçay's compound possesses the formula he assigned to it.

We then prepared *diethoxydichlorotitanium* by refluxing titanium tetrachloride and ethyl alcohol for several hours and distilling the products of the reaction under reduced pressure. One product, obtained as an oil which yielded a white solid, was the required substance $TiCl_2(OEt)_2$. When this was dissolved in the minimum amount of warm alcohol, and then cooled, a mass of needle-shaped, colourless crystals separated; these proved to be $TiCl_2(OEt)_2,EtOH$, identical in crystalline form and composition with Demarçay's compound. These results appear to us to prove that formula (II) is correct, and that the compound is not of the type supposed by Demarçay.

Our experiments have been extended to the reactions between titanium tetrachloride and methyl, *iso*propyl, and *iso*butyl alcohols. In every instance we have obtained a *compound* of the formula $TiCl_2(OR)_2,ROH$. Furthermore, by heating these substances under reduced pressure, we isolated in all cases, except that of the compound $TiCl_2(OMe)_2,MeOH$, derivatives without alcohol of crystallisation, *viz.*, $TiCl_2(OR)_2$.

The dialkoxydichlorotitaniums which we have isolated are white solids very soluble in alcohol and to a smaller extent in ether, acetone, and other organic solvents; also they are rapidly hydrolysed in air and dissolve in water instantly yielding clear solutions. By treating two of these compounds, $Ti(OC_4H_9)_2Cl_2$ and $Ti(OEt)_2Cl_2$, with ethyl and methyl alcohol respectively, we succeeded in producing $Ti(OC_4H_9)_2Cl_2,EtOH$ and

$$Ti(OC_4H_9)_2Cl_2,MeOH$$

on the one hand, and $Ti(OEt)_2Cl_2,EtOH$ and $Ti(OEt)_2Cl_2,MeOH$ on the other.

It seems reasonable to conclude that compounds of the general type $TiCl_2(OR)_2$ have a great tendency to combine with alcohol, and crystallise from this solvent as alcoholates.

From the reaction between tetraethoxytitanium and acetyl chloride in the appropriate proportion, we have prepared the new *compound* $Ti(OEt)_3Cl$ as a pale yellow viscous liquid: $Ti(OEt)_4 + CH_3{\cdot}COCl = Ti(OEt)_3Cl + CH_3{\cdot}CO_2Et$. From alcohol it crystallises as colourless needles with the composition $TiCl(OEt)_3,EtOH$.

The following interesting series of compounds are now known: $Ti(OEt)_4$, $Ti(OEt)_3Cl$, $Ti(OEt)_2Cl_2$. We attempted to prepare $Ti(OEt)Cl_3$ but without success.

Experimental.

Throughout this investigation all-glass apparatus was employed, and the use of rubber and corks eliminated.

Tetramethoxytitanium.—This compound was prepared according to the method of Bischoff and Adkins (*loc. cit.*). Sodium (12·5 g.) was dissolved in methyl alcohol (150 c.c.) and titanium tetrachloride (25 g.) added, the mixture being well cooled in ice. After an hour's refluxing, the mixture was distilled under reduced pressure. At about 300°/18 mm., a sublimate was formed [Found: Ti, 28·02, 27·98. Calc. for $Ti(OMe)_4$: Ti, 27·90%].

Tetraethoxytitanium.—This was prepared by a similar method (*loc. cit.*), 185 g. of ethyl alcohol being used; the mixture was refluxed at 80—100° for 3 hours and distilled. At 140—150° a

colourless liquid was collected (b. p. 142°/18 mm.) [Found : Ti, 20·99, 21·01. Calc. for $Ti(OEt)_4$: Ti, 21·05%].

Dimethoxydichlorotitanium.—To dry methyl alcohol (40 c.c.), titanium tetrachloride (25 g.) was slowly added, moisture being excluded during the reaction. The pale yellow liquid produced was then distilled under reduced pressure at 70—80°. The residue in the flask solidified on standing to give a white solid which was dried over phosphoric oxide [Found : Ti, 22·82, 22·94; Cl, 33·01, 32·96. $TiCl_2(OCH_3)_2,CH_3{\cdot}OH$ requires Ti, 22·53; Cl, 33·34%].

Triethoxymonochlorotitanium.—Tetraethoxytitanium (13 g.) and acetyl chloride (4·5 g.) were refluxed together at 70—80° for 2½ hours. The mixture was then fractionally distilled, and at 190—200° a pale yellow liquid was collected (b. p. 176°/18 mm.); on cooling this became viscous [Found : Ti, 21·89, 21·96; Cl, 16·28, 16·26. $TiCl(OC_2H_5)_3$ requires Ti, 21·97; Cl, 16·25%].

To this product (5 g.) was added ethyl alcohol (5 c.c.), and from the solution a mass of colourless needles separated. These were washed with alcohol and dried over phosphoric oxide [Found : Ti, 18·06, 18·11; Cl, 13·37, 13·47. $TiCl(OC_2H_5)_3,C_2H_5{\cdot}OH$ requires Ti, 18·14, Cl, 13·42%]. A further quantity (5 g.) was similarly treated with alcoholic hydrogen chloride (5 c.c.). Colourless needles crystallised on standing, and proved to have the same composition (Found : Ti, 18·01, 17·97; Cl, 13·72, 13·61%).

Diethoxydichlorotitanium.—(i) Triethoxymonochlorotitanium (10 g.) and acetyl chloride (3·7 g.) were refluxed for 2 hours. Ethyl acetate was removed, and upon distillation under reduced pressure at 150—160° a pale yellow liquid was obtained (b. p. 142°/18 mm.), which on cooling gave a pale yellow solid [Found : Ti, 22·81, 22·72; Cl, 33·84, 33·68. $TiCl_2(OC_2H_5)_2$ requires Ti, 22·97; Cl, 33·98%].

(ii) To ethyl alcohol (25 g.) in an ice-cooled flask titanium tetrachloride (25 g.) was added, and the mixture refluxed at 80—100° for 24 hours. Upon cooling it gave a white viscous mass which was then fractionally distilled. At 180—200° a pale yellow liquid was obtained (b. p. 142°/18 mm.), which on cooling gave a white solid of the same composition as above (Found : Ti, 22·88, 22·91; Cl, 33·81, 33·75%).

To this product (4 g.) warm methyl alcohol (3 c.c.) was added, and on cooling, a mass of needle-shaped colourless crystals separated. After being washed with alcohol and dried over phosphoric oxide, they had the composition $Ti(OEt)_2Cl_2,MeOH$ (Found : Ti, 19·87, 19·78; Cl, 29·39, 29·30. $TiO_3C_5H_{14}Cl_2$ requires Ti, 19·92; Cl, 29·46%).

From a solution of diethoxydichlorotitanium (4 g.) in warm ethyl alcohol (4 c.c.) a mass of needle-shaped colourless crystals was obtained; after being purified as above, they had the composition $Ti(OEt)_2Cl_2,EtOH$ (Found : Ti, 18·76, 18·71; Cl, 27·74, 27·71. Calc. for $TiO_3C_6H_{16}Cl_2$: Ti, 18·82; Cl, 27·85%). This substance was also prepared by Demarçay's method (*loc. cit.*) : To ethyl alcohol (25 g.), titanium tetrachloride (25 g.) was added, and the mixture distilled at 80—100° under reduced pressure. The solid product was dissolved in warm ethyl alcohol. On cooling, needle-shaped colourless crystals separated, which were removed, washed with alcohol and dried over phosphoric oxide (Found : Ti, 18·78, 18·76; Cl, 27·57, 27·62%).

Diisopropoxydichlorotitanium.—Titanium tetrachloride (25 g.) was added to *iso*propyl alcohol (33 g.), the mixture refluxed for 9 hours, and fractionally distilled; the pale yellow distillate (b. p. 160°/18 mm.), upon cooling, gave a white solid [Found : Ti, 20·14, 20·11; Cl, 29·87, 29·90. $TiCl_2(OC_3H_7)_2$ requires Ti, 20·25; Cl, 29·96%].

When this product (3 g.) was dissolved in *iso*propyl alcohol (5 c.c.), colourless, needle-shaped crystals separated which, after being washed with ether and dried over phosphoric oxide, had the composition $TiCl_2(OC_3H_7)_2,C_3H_7OH$ (Found : Ti, 15·97, 15·91; Cl, 23·85, 23·81. $TiO_3C_9H_{22}Cl_2$ requires Ti, 16·15; Cl, 23·91%). The same componnd was also prepared by adding titanium tetrachloride (25 g.) to *iso*propyl alcohol (33 g.) and refluxing for 9 hours; the white solid which separated on cooling was purified as in the preceding case (Found : Ti, 16·01, 15·95; Cl, 23·82, 23·76%).

Diisobutoxydichlorotitanium.—Titanium tetrachloride (25 g.) was added to *iso*butyl alcohol (50 g.), the mixture being refluxed for 24 hours at 80—100°; fractional distillation at 190—210° afforded a pale yellow liquid (b. p. 184°/18 mm.), which set to a white solid [Found : Ti, 17·92, 17·90; Cl, 26·67, 26·70. $TiCl_2(OC_4H_9)_2$ requires Ti, 18·11; Cl, 26·80%]. This *compound* (5 g.) was dissolved in warm methyl alcohol (4 c.c.), and a mass of colourless needles separated; after purification (ether; phosphoric oxide) these had the composition $TiCl_2(OC_4H_9)_2,MeOH$ (Found : Ti, 16·05, 16·05; Cl, 23·71, 23·82. $TiO_3C_9H_{22}Cl_2$ requires Ti, 16·15; Cl, 23·91%). Similarly, ethyl alcohol (5 c.c.) afforded the *alcoholate* $TiCl_2(OC_4H_9)_2,EtOH$ (Found : Ti, 15·40,

15·34; Cl, 22·71, 22·78. $TiO_3C_{10}H_{24}Cl_2$ requires Ti, 15·43; Cl, 22·83%), and *iso*butyl alcohol (5 c.c.) the analogous $TiCl_2(OC_4H_9)_2C_4H_9OH$ (Found: Ti, 13·98, 14·07; Cl, 20·88, 20·90. $TiO_3C_{12}H_{28}Cl_2$ requires Ti, 14·16; Cl, 20·94%). The last compound was also prepared as follows. To *iso*butyl alcohol (50 g.), titanium tetrachloride (25 g.) was added, and the mixture distilled under reduced pressure at 100—110°. The solid residue was dissolved in warm *iso*butyl alcohol, and the solution cooled; the white mass was washed with ether and dried over phosphoric oxide (Found: Ti, 13·72, 13·68; Cl, 20·81, 20·88%).

THE UNIVERSITY, BIRMINGHAM, 15. [*Received, April 7th, 1936.*]

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147. *Monomethyl Hexoses. Part II. A Revision of the Constitutions of the Supposed 4-Methyl Galactose and 4-Methyl Mannose of Pacsu, and their Formulation as 6-Methyl Galactose and 2-Methyl Mannose respectively.*

By JOHN MUNRO and EDMUND G. V. PERCIVAL.

SCHINLE (*Ber.*, 1931, **64**, 2361) proved that the monomethyl glucose prepared from glucosedibenzylmercaptal was 2-methyl glucose and not 4-methyl glucose as stated by Pacsu (*Ber.*, 1925, **58**, 1455). Since a monomethyl galactose prepared by a similar method was described as 4-methyl galactose by Pacsu and Löb (*Ber.*, 1929, **62**, 3104), it became of importance to review this case also. The crystalline monomethyl galactose of Pacsu and Löb (*loc. cit.*) was prepared and a preliminary examination of the phenylosazone indicated that it was a true monomethyl galactosazone, thus excluding substitution in position 2. 3-Methyl galactose is excluded by the melting point of its phenylosazone, so that only positions 4, 5, and 6 remain available for the assignment of the methoxyl residue. Complete methylation afforded tetramethyl galactopyranose, isolated as the crystalline anilide, thus excluding substitution in position 5. Proof that position 4 also was unmethylated was obtained by oxidation of the free sugar and the isolation of a monomethyl γ-galactonolactone, easily recognised by its negative specific rotation and slow rate of hydrolysis (Haworth, "Constitution of Sugars," London, 1929). Further confirmation that both positions 4 and 5 were free was secured by following the progress of glycoside formation at 20° according to Levene, Raymond, and Dillon (*J. Biol. Chem.*, 1932, **95**, 699), which indicated that both galactofuranosides and galactopyranosides were formed (see Table II). Close agreement was observed between the physical constants of the free sugar, its phenylhydrazone and phenylosazone with those recorded by Freudenberg and Smeykal (*Ber.*, 1926, **59**, 100) for 6-methyl galactose and its corresponding derivatives, of which the structnre appears to be well established by the method of preparation from diacetone galactopyranose. A direct comparison of the compounds concerned confirmed this view (see Table I) and it is considered therefore that the "4"-methyl galactose of Pacsu and Löb (*loc. cit.*) must now be described as 6-methyl galactose.

There is also dubiety about the assignment of the structure of 4-methyl mannose to the sugar isolated by Pacsu and v. Kary (*Ber.*, 1929, **62**, 2811) and an examination of their paper reveals the fact that the osazone prepared from this substance may have been glucosazone. There is no possibility that it is identical with 4-methyl glucosazone, since this has widely different properties (Munro and Percival, J., 1935, 873).

According to Pacsu and v. Kary (*loc. cit.*) a single methylation of diacetone mannosedibenzylmercaptal, followed by hydrolysis to remove acetone, caused the separation of a crystalline product described as "4"-methyl mannosedibenzylmercaptal, m. p. 188°, $[\alpha]_D^{18°}$ — 106·6° (pyridine), together with a syrup. Many attempts to reproduce this result failed. In every case we obtained with the syrup crystalline products, m. p. 118,° $[\alpha]_D$ — 48°, which were apparently homogeneous but on analysis invariably showed a methoxyl content of about one-third of the theoretical for a monomethyl mannosedibenzylmercaptal. By repeated acetone condensation, methylation, and hydrolysis it was found possible to increase the methoxyl content of the crystals to 80% of the theoretical amount. Con-

TABLE I.

Substance.	M. p.	Rotatory power.	Reference.
(1) "4"-Methyl galactose	118°	$[\alpha]_D^{18°}$ +117° ⟶ +68° (after 3 hrs. in water)	(a) Pacsu and Löb, *loc. cit.*
(2) "4"-Methyl galactose	118—119	$[\alpha]_D^{20°}$ +120 ⟶ +70 (after 6 hrs. in water)	Present authors according to (a).
(3) 6-Methyl galactose	122—123	$[\alpha]_D^{20°}$ +112 (4 mins.) ⟶ +66 (after 6 hrs. in water)	Present authors according to (b).
(4) 6-Methyl galactose	128	$[\alpha]_{5780}^{20°}$ +114 (5 mins.) ⟶ +77 (after 3 hrs. in water)	(b) Freudenberg and Smeykal, *loc. cit.*
Mixture of (2) and (3)	120		
(5) "4"-Methyl galactose phenylosazone	194—195	$[\alpha]_D^{18°}$ +131 (in pyridine)	(a)
(6) "4"-Methyl galactose phenylosazone	200	$[\alpha]_D^{20°}$ +144 (in pyridine)	Present authors according to (a).
(7) 6-Methyl galactose phenylosazone	200—201	$[\alpha]_D^{20°}$ +141 (in pyridine)	Present authors according to (b).
(8) 6-Methyl galactose phenylosazone	204—205	$[\alpha]_{5780}^{20°}$ +135 (in pyridine)	(b)
Mixture of (6) and (7)	200		
(9) "4"-Methyl galactose phenylhydrazone	179	$[\alpha]_D^{20°}$ +24·4 ⟶ +14·1 (after 24 hrs. in pyridine)	Present authors.
(10) 6-Methyl galactose phenylhydrazone	179	$[\alpha]_D^{20°}$ +23·5 ⟶ +14·8 (after 24 hrs. in pyridine)	Present authors according to (b).
(11) 6-Methyl galactose phenylhydrazone	182—183	$[\alpha]_D^{20°}$ +14·5 (in pyridine)	(b)
Mixture of (9) and (10)	179		
(12) 3-Methyl galactose phenylosazone	176—179		Robertson and Lamb, J., 1934, 1321.

version into the free sugar yielded a product which was still contaminated with free mannose as shown by the isolation of pure mannosephenylhydrazone in quantity corresponding with the amount of mannose (20%) calculated from the analytical results. No methylated phenylhydrazone could be isolated during many attempts and there is thus reason to suppose that the "4"-methyl mannosephenylhydrazone (m. p. 179°) of Pacsu and v. Kary was indeed mannosephenylhydrazone (m. p. 183—184°). After removal of the mannosephenylhydrazone, heating produced three crops of an osazone of no methoxyl content, identical with glucosazone.

The results of Pacsu and v. Kary, however, do not depend on a study of the crystalline "4"-methyl mannosedibenzylmercaptal but are based on an examination of the sugar obtained on simultaneous removal of acetone and mercaptan residues from diacetone "4"-methyl mannosedibenzylmercaptal. The syrup obtained after one methylation, following the removal of the crystalline mixture of low methoxyl content previously described, had a slightly higher methoxyl content (17·5%) than is required for monomethyl mannose, but in this case also crystalline mannosephenylhydrazone was readily isolated. An examination of the osazones produced on heating after removal of the mannosephenylhydrazone revealed that they were specimens of glucosazone contaminated with small amounts of methylated by-products. It is considered, therefore, that the syrup was 2-methyl mannose admixed with mannose and some polymethylated derivatives.

The structures of the acetone compounds of the dibenzylmercaptals of glucose, galactose, and mannose, assigned by Pacsu, require revision in the light of the facts now known and this problem is under investigation.

EXPERIMENTAL.

Preparation of "4"-Methyl Galactosedibenzylmercaptal.—The methods described by Pacsu and Löb (*loc. cit.*) were followed for the preparation. Galactosedibenzylmercaptal (20 g.) yielded fine needles of "4"-methyl galactosedibenzylmercaptal (7 g.), m. p. 130°, $[\alpha]_D^{20°}$ − 27° in pyridine (*c*, 3·3) (Found: C, 59·5; H, 6·7; OMe, 6·7. Calc. for $C_{21}H_{28}O_5S_2$: C, 59·4; H, 6·6; OMe, 7·3%).

Isolation of "4"-Methyl Galactose.—The mercaptan residues were removed from "4"

methyl galactosedibenzylmercaptal (10 g.) as described for 4-methyl glucose (Munro and Percival, *loc. cit.*) to yield a syrup (3·6 g.) which slowly crystallised; m. p. 118° (Found: C, 43·7; H, 7·4; OMe, 13·9. Calc. for $C_7H_{14}O_6$: C, 43·4; H, 7·2; OMe, 16·0%).

"4"-*Methyl Galactosephenylosazone*.—"4"-Methyl galactose (0·3 g.), dissolved in water (1·5 c.c.), was heated at 100° for 1 hour with phenylhydrazine (1·5 g.) and acetic acid (0·5 g.). On recrystallisation from alcohol (needles) it showed m. p. 200°, $[\alpha]_D^{20°}$ + 144° in pyridine (*c*, 0·4) (Found: OMe, 7·9; N, 15·1. Calc. for $C_{19}H_{24}O_4N_4$: OMe, 8·3; N, 15·0%).

"4"-*Methyl Galactosephenylhydrazone*.—"4"-Methyl galactose (0·2 g.) was dissolved in water (0·5 c.c.), and phenylhydrazine (0·5 g.) added. Crystallisation began after a few hours and was complete in 2 days; m. p. 179° after recrystallisation from methyl alcohol, $[\alpha]_D^{20°}$ + 24·4° (initial value), falling to 14·1° in 24 hours, in pyridine (*c*, 0·8) (Found: OMe, 10·2; N, 9·8. Calc. for $C_{13}H_{20}O_5N_2$: OMe, 10·9; N, 9·85%).

Complete Methylation of "4"-*Methyl Galactose*.—In preparing the fully methylated galactose we employed a series of reactions precisely similar to that for the complete methylation of 4-methyl glucose (J., 1935, 873), namely, tetra-acetyl "4"-methyl galactose ⟶ triacetyl "4"-methyl galactosidyl bromide ⟶ triacetyl "4"-methyl methylgalactoside, in the hope of isolating some intermediate crystalline product, but without success.

Triacetyl "4"-methyl methylgalactoside (1·4 g.), dissolved in acetone (30 c.c.), was methylated with methyl sulphate (15 c.c.) and sodium hydroxide solution (40 c.c., 30%). The syrup obtained in the usual way was twice methylated with methyl iodide (10 c.c.) and silver oxide (2·5 g.) during 6 hours and gave on distillation at 115° (bath temp.)/0·04 mm. an oil (0·45 g.), $n_D^{15°}$ 1·4500. The galactoside (0·44 g.) was heated on a water-bath at 80° with 8% hydrochloric acid (4 c.c.) for 2 hours (cf. Irvine and Cameron, J., 1904, 85, 1071), the acid neutralised with barium carbonate, and the filtered solution evaporated to dryness (diminished pressure). On extraction of the solid with boiling ether, a clear syrup (0·4 g.) of tetramethyl galactose was obtained. This (0·13 g.) was digested with aniline (0·4 g.) and alcohol (1 c.c.) at 100° for 3 hours. 2 : 3 : 4 : 6-Tetramethyl galactose anilide crystallised, on cooling, in long needles (0·1 g.), m. p., after recrystallisation from alcohol, 192—193°, unchanged by an authentic specimen; $[\alpha]_D^{20°}$ − 71° (initial) in acetone (*c*, 0·2) (Found: OMe, 40·8; N, 4·5. Calc. for $C_{16}H_{25}O_5N$: OMe, 39·9; N, 4·5%).

Oxidation of "4"-*Methyl Galactose to* "4"-*Methyl γ-Galactonolactone*.—"4"-Methyl galactose (1·5 g.), dissolved in water (10 c.c.), was oxidised with bromine (3 c.c.) at 35° until all reducing action had ceased (48 hours). The excess of bromine was removed by aeration, and the solution neutralised with silver carbonate. The lactone (1·0 g.) was obtained by precipitation of the silver with hydrogen sulphide, filtration, and evaporation to dryness (diminished pressure), followed by heating at 100° in a vacuum (2 hours); $[\alpha]_D^{20°}$ − 43° (10 mins.), − 40° (9 days; const.). 0·0183 G. required 1·32 c.c. 0·01*N*-sodium hydroxide for neutralisation of the free acid and 8·95 c.c. for complete neutralisation (calc., 9·5 c.c.), giving 85% lactone at equilibrium (cf. Freudenberg and Smeykal, *loc. cit.*) (Found: OMe, 14·4. Calc. for $C_7H_{12}O_6$: OMe, 16·1%).

Glycoside Formation with "4"-*Methyl Galactose at* 20°.—The method employed for examining the rate of glycoside formation at room temperature was essentially that described by Levene, Raymond, and Dillon (*loc. cit.*). From a 0·5% methyl-alcoholic hydrogen chloride solution containing "4"-methyl galactose (approximately 3 mg. per 0·5 c.c.), two samples of 0·5 c.c. were withdrawn at intervals. One was treated with 0·5 c.c. of 0·4*N*-sodium carbonate and water (3 c.c.), and kept for 15 minutes with 0·3*N*-sodium hydroxide (1 c.c.) and 0·03*N*-iodine (5 c.c.). The excess of iodine, liberated with 5*N*-sulphuric acid (0·2 c.c.), was titrated with 0·01*N*-sodium thiosulphate. The second sample was heated for 10 minutes at 100° with water (2 c.c.) and 0·26*N*-hydrochloric acid (1 c.c.). After immediate cooling, the acid was neutralised with the calculated amount of 0·4*N*-sodium carbonate, and the solution kept for 15 minutes with 0·3*N*-sodium hydroxide (1 c.c.) and 0·03*N*-iodine (5 c.c.). The excess of iodine was determined as before. The difference between these titrations and blank experiments carried out under similar conditions gave the figures for the reducing values. A correction of 21% had to be made on the reducing values obtained after hydrolysis with 0·1*N*-hydrochloric acid owing to the hydrolysis of the "4"-methyl methylgalactopyranoside under these conditions, this being determined by a separate experiment.

At the end of 48 hours, the sugar is transformed into a mixture of galactofuranosides and galactopyranosides in approximately equal amounts.

6-*Methyl Galactose*.—The compound was prepared as described by Freudenberg and Smeykal (*loc. cit.*). It was readily obtained crystalline, but repeated crystallisation from alcohol-ether failed to raise the m. p. above 123°. M. p. in admixture with "4"-methyl galactose 120°;

TABLE II.

Time.	$0{\cdot}01N$-$Na_2S_2O_3$, c.c. Before hydrolysis.	After hydrolysis.	Free sugar, %. Before hydrolysis.	After hydrolysis.	Corrected.	Free sugar, %.	Furanoside, %.	Pyranoside, %.
0	2·13	2·39	100	100	100	100	—	—
15 mins.	1·68	2·46	78·9	102·9	100	78·9	21·1	—
30 ,,	1·60	2·31	75·1	96·6	95·8	75·1	20·7	4·2
1 hr.	1·38	2·24	64·8	93·7	92·1	64·8	27·3	7·9
2 hrs.	1·05	2·10	49·3	87·8	84·8	49·3	35·5	15·2
4 ,,	0·78	1·93	36·6	80·8	76·0	36·6	39·4	24·0
24 ,,	0·20	1·40	9·4	58·6	48·2	9·4	38·8	51·8
48 ,,	0·11	1·52	6·6	63·6	54·5	6·6	47·9	45·5

$[\alpha]_D^{20°}$ + 112° in water (*c*, 1), 4 minutes after dissolution, + 66° after 6 hours (constant). 6-Methyl galactosephenylhydrazone prepared in the usual way and recrystallised four times from methyl alcohol had m. p. 179°, unchanged by " 4 "-methyl galactosephenylhydrazone; $[\alpha]_D^{20°}$ +23·5° in pyridine (*c*, 1), +14·8° (after 24 hrs.; const.). 6-Methyl galactosephenylosazone, recrystallised from alcohol, showed m. p. 200° alone or in admixture with " 4 "-methyl galactosephenylosazone; $[\alpha]_D^{20°}$ +141° in pyridine (*c*, 0·5).

d-*Mannosedibenzylmercaptal.*—The method of preparation employed by Pacsu and v. Kary (*loc. cit.*) was followed, and the product obtained had the properties ascribed to it by those authors; m. p. 126°, $[\alpha]_D^{20°}$ −32·6° in pyridine (*c*, 0·7).

Preparation of the Acetone Compound of Mannosedibenzylmercaptal.—Mannosedibenzylmercaptal was condensed with acetone as described by Pacsu and v. Kary (*loc. cit.*). The acetone compound, after preliminary heating for some hours at 100°/15 mm., was heated for 20 minutes at 110° (bath temp.)/0·07 mm. The product gave $[\alpha]_D^{20°}$ +79° in acetylene tetrachloride (*c*, 2·0) ($[\alpha]_D^{20°}$ +66° *in acetylene tetrachloride recorded by* Pacsu *and* v. Kary, *loc. cit.*).

Methylation of the Acetone Compound of Mannosedibenzylmercaptal.—The methods of Pacsu and v. Kary (*loc. cit.*) were followed to yield a syrup, from which the acetone groups were removed as before. The white crystalline product was recrystallised from alcohol; m. p. 118°, and a mixed m. p. with mannosedibenzylmercaptal showed a depression of 1°. $[\alpha]_D^{20°}$ − 48° in pyridine (*c*, 1) (Found : OMe, 2·4. Calc. for $C_{21}H_{28}O_5S_2$: OMe, 7·3%). These results were twice confirmed.

Removal of the Mercaptan Residue and Isolation of the Reducing Sugar.—The mercaptan groups were removed, as described in the case of the galactose derivatives, to yield a reducing syrup which failed to crystallise (Found : OMe, 5·2. Calc. for $C_7H_{14}O_6$: OMe, 16·0%).

Attempted Separation of " 4 "-Methyl Mannose Derivatives.—The glycoside was prepared by the method of Bott, Haworth, and Hirst (J., 1930, 2653) and acetylated with pyridine and acetic anhydride in the usual way. The acetate, however, distilled in one fraction at 185° (bath temp.)/0·07 mm. and analysis showed it to be a mixture of tetra-acetyl methylmannoside and triacetyl monomethyl methylmannoside (Found : OMe, 11·1%).

Increase in the Methoxyl Content of the Partly Methylated Mannosedibenzylmercaptal.—Two consecutive methylations with methyl sulphate and sodium hydroxide without an intermediate hydrolysis to isolate the crystals of the methyl mannosemercaptal failed to produce any increase in the methoxyl content, but if the crystals and syrup formed after the methylation and hydrolysis of the acetone compound of mannosedibenzylmercaptal (1·5 g.) were condensed again with acetone and concentrated sulphuric acid and then remethylated and hydrolysed as before, the crystals (0·5 g.) had a higher methoxyl content. Pure monomethyl mannosedibenzylmercaptal, however, could not be produced by this method; the best sample obtained showed m. p. 117°, $[\alpha]_D^{20°}$ − 54° in pyridine (*c*, 0·5), m. p. on admixture with mannosedibenzylmercaptal 116° (Found : OMe, 5·8. Calc. for $C_{21}H_{28}O_5S_2$: OMe, 7·3%).

Preparation of the Partly Methylated Mannose.—The sugar was obtained as a reducing syrup after removal of the mercaptan residnes with mercuric chloride; $[\alpha]_D^{20°}$ + 4·3° in water (*c*, 1·7) (Found : OMe, 11·7. Calc. for $C_7H_{12}O_6$: OMe, 16·0%).

Phenylhydrazone Formation.—The syrup (0·06 g.), dissolved in water (1 c.c.), was mixed with phenylhydrazine (0·5 g.) and glacial acetic acid (0·05 g.). In a few seconds a white crystalline precipitate appeared and was filtered off. After ½ hour a further crop was removed. No more crystals appeared after 2 days. The phenylhydrazone (0·02 g.) was washed with cold

acetone and dried; m. p. 183—184° alone or in admixture with a specimen prepared directly from mannose (Found: OMe, nil; N, 10·3. Calc. for $C_{12}H_{18}O_5N_2$: N, 10·4%).

If it be assumed that the phenylhydrazone formation from mannose is almost quantitative, 0·02 g. of phenylhydrazone would be produced from 0·013 g. of mannose. The monomethyl mannose is therefore present to the extent of 75—80%, which agrees with the previous analytical results.

After 2 days the clear solution was heated for 1 hour at 100° with glacial acetic acid (0·1 c.c.) and a crystal of sodium bisulphite (to retard tar formation). The osazone which formed (0·01 g.) was washed with cold acetone; m. p. 204° alone or in admixture with an authentic specimen of glucosazone (Found: OMe, nil). The filtrate on further heating yielded a second and a third crop of osazone, neither of which contained methoxyl (total yield, 0·02 g.). Since mannose gives a 30% yield of osazone under these conditions, it is clear that the glucosazone now isolated must have been formed from that portion of the syrup containing methoxyl.

Examination of the Syrup "2 : 3-5 : 6"-Diacetone "4"-Methyl Mannosedibenzylmercaptal.—The acetone compound of mannosedibenzylmercaptal (5 g.) was methylated once as before with methyl sulphate and sodium hydroxide. After extraction the product was hydrolysed with hydrochloric acid, and the crystalline, partly methylated, mannosedibenzylmercaptal obtained. The crystals (0·45 g.) were separated as completely as possible from syrup (1·8 g.) with ether and were identical with the mixtures of low methoxyl content (OMe, 2·8%) previously described; m.p. 117°, $[\alpha]_D^{20°}$ − 48° in pyridine (*c*, 1).

Removal of Mercaptan Residues from the Syrup.—The syrup (1·5 g.) was treated as before with mercuric chloride in acetone to yield a reducing syrup (0·5 g.) having $[\alpha]_D^{20°}$ + 9·6° in water (*c*, 3) (Found: OMe, 17·5. Calc. for $C_7H_{14}O_6$: OMe, 16·0%). The syrup (0·4 g.) on treatment with phenylhydrazine acetate rapidly gave mannosephenylhydrazone (0·1 g.), m. p. 183° (Found: OMe, nil; N, 10·6. Calc. for $C_{12}H_{18}O_5N_2$: N, 10·4%).

Preparation of Osazone.—The filtrate from the hydrazone was subjected to osazone formation. The two crops of osazone (0·07 g.), m. p. 180—185° (OMe, 2%), obtained proved to be glucosazone contaminated with a small amount of methylated material.

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148. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part V. Further Substituted Benzoic and Phenylacetic Acids.*

By J. FREDERICK J. DIPPY and REGINALD H. LEWIS.

THE investigation of the dissociation constants of monocarboxylic acids begun by Dippy and Williams (Parts I—III; J., 1934, 161, 1888; 1935, 343) was concerned mainly with monosubstituted (methyl, methoxyl, halogen, and nitroxyl) benzoic and phenylacetic acids, and had as its object the study of the polar influences of common substituents attached to the aromatic nucleus. The present work provides data for further members of these series of acids.

The following table sets out the Λ_0 data, and the mean classical and thermodynamic dissociation constants for the twelve newly examined acids. The last column records former determinations of $10^5K_{class.}$ for the benzoic acids. These data, extracted from the literature, relate to experiments embodying the older, less reliable technique; nowhere are thermodynamic constants recorded.

Our data for *m*- and *p*-toluic acids remove the doubt which existed regarding their relative strengths. The approximate constants for the *p*-acid due to White and Jones and to Schaller were much lower than that of Ostwald, who found the two acids to have identical strengths. It can now be accepted that the *p*-acid is decidedly the weaker.

Acid.	Λ_0 (Na salt).	Λ_0 (acid).	$10^5K_{class.}$	$10^5K_{therm.}$	Older values.
m-Toluic	79·3,* 80·1 *	379·3	5·47	5·35	5·6—5·7,[1] 5·14 [2]
p-Toluic	80·0,* 80·2 *	379·7	4·32	4·24	5·1,[2] 4·42,[3] 4·3—4·4 [1]
m-Methoxybenzoic	79·6,* 79·8 *	379·3	8·36	8·17	8·8 [4]
o-Fluorobenzoic	82·2, 83·25	382·3	55·7	54·1	30 [5]
m-Fluorobenzoic	82·1, 82·1	381·7	$14{\cdot}0_5$	$13{\cdot}6_5$	13·6,[2] 14 [5]
m-Bromobenzoic	80·2,* 80·6 *	380·0	15·7	15·4	13·7,[2] 15 [6]
o-Iodobenzoic	79·4, 79·8	379·2	139	137	132,[7] 137 [3]
m-Iodobenzoic	80·15, 81·05	380·2	14·2	14·1	16·3 [8]
m-Nitrobenzoic	83·1, 83·2	382·8	33·1	32·1	34·0,[9] 36·4 [3]
p-Nitrobenzoic	82·9, 83·2	382·7	38·5	37·6	39·6,[2] 40—43 [10]
o-Iodophenylacetic	77·0, 77·2	376·7	9·39	9·16	—
m-Iodophenylacetic	79·6	379·2	7·05	6·93	—

* These values were obtained with solutions prepared from the solid salts.

[1] White and Jones, *Amer. Chem. J.*, 1910, **44**, 184. [2] Ostwald, *Z. physikal. Chem.*, 1889, **3**, 418. [3] Schaller, *Z. physikal. Chem.*, 1898, **25**, 517. [4] Pip, I.C.T., 1929. [5] Slothouwer, *Rec. trav. chim.*, 1914, **33**, 324. [6] Smith and Jones, *Amer. Chem. J.*, 1913, **50**, 1. [7] Askenasy and Meyer, *Ber.*, 1893, **26**, 1354. [8] Bethmann, *Z. physikal. Chem.*, 1890, **5**, 385. [9] Euler, *ibid.*, 1896, **21**, 257. [10] Wightman and Jones, *Amer. Chem. J.*, 1911, **46**, 90.

The new classical constant for *m*-fluorobenzoic acid is in harmony with those obtained previously, but that for the *o*-acid is almost twice as great as Slothouwer's. Our value for the *m*-bromo-acid is in reasonable agreement with that of White and Jones, and the present classical constants for the *o*- and *m*-iodo- and *m*- and *p*-nitro-benzoic acids differ considerably from the earlier values which, by comparison, are low for the first acid, and distinctly high for the other three.

The Measurement of Λ_0, *and the Mobilities of Ions.*—The method of computing Λ_0 has been described in Parts I—III, and illustrated by reference to sodium acetate and sodium *o*-chlorobenzoate. The plot of $\Lambda_{uncorr.}$ (and $\Lambda_{corr.}$) against $\sqrt{c}$ in each of these two cases yielded curves diverging perceptibly at concentrations of 0·0020—0·0015*M*, and the straight line possessing the Onsager slope approached nearer to the uncorrected than to the corrected curve. These observations hold true for the present sodium salt measurements; the form of the curves and the relative disposition of the Onsager straight line are reproduced from system to system in a strikingly consistent manner.

This method is necessarily somewhat approximate, since it represents an attempt to replace the usual tedious method of " solvent correction." Its use, however, has been fully justified in a repudiation of certain criticisms levelled at it (Dippy and Williams, *Chem. and Ind.*, 1935, **54**, 535).

On account of lack of material, measurement of only one " run " was made on sodium *m*-iodophenylacetate, and, as in previous cases, the isolation of the salts of the nitro-acids was impossible.

A fairly comprehensive survey of the mobilities of substituted benzoic and phenylacetic anions is now possible. In the main, they are decidedly lower than the mobilities of the unsubstituted ions; this to be expected on the grounds of increased size. For the same reason, the mobilities of the halogen-substituted anions are arranged, for the most part, in both series of acids in the order I < Br < Cl < F. The size of the anion, however, does not seem to be the only factor affecting its movement; *e.g.*, the methoxyl substituent appears to depress abnormally the mobilities of benzoic and phenylacetic ions, and similarly for methyl in the benzoic ion. It is evident from the data that, on the subject of the mobilities of organic anions, only broad generalisations can be made.

Calculation of $K_{therm.}$.—Examination of the conductivity runs made on *o*-iodobenzoic acid (see tables) shows that at high dilutions $K_{class.}$ becomes smaller than $K_{therm.}$. It is the first instance of this feature encountered so far in this investigation, yet on the basis of the calculation it is to be expected in an acid of this order of strength. *o*-Nitrobenzoic acid should provide a still more pronounced example, for with stronger acids the differences become vast; *e.g.*, for iodic acid at 0·0005*N*, $K_{therm.} = 1{\cdot}8 \times 10^{-1}$ and $K_{class.} = 0{\cdot}5 \times 10^{-1}$ (see Davies, " The Conductivity of Solutions," 1933, p. 106).

Experimental.

The measurements were conducted on aqueous solutions at 25° as already described (Parts I—III). In order to eliminate as far as possible the shunt method of determining high resistances (2500 ohms), a Cambridge low-inductance decade resistance unit of 10,000 ohms (maximum) was added to the resistance arm of the bridge. The shunt method is now employed only in measuring the conductance of the solvent.

Since the last series of acids were measured, four new cells have been added to our complement, consequently two new cells are now reserved for salt solutions alone, and three for acid solutions. The electrodes of these cells are all coated with platinum black. The water is measured in a cell of low constant, possessing bright platinum electrodes. All the cells are of the bottle type described in Part I, and their characteristics are summarised as follows:

		Electrodes.		
	Capacity (c.c.).	Area (sq. cm.).	Distance apart (cm.).	Approx. cell constant.
Acid cell 1	30	3·25	1·0	0·136
2	30	4·5	0·45	0·073
3	35	5·8	0·4	0·053
Salt cell 1	35	3·4	0·8	0·126
2	35	3·8	0·45	0·077
Water cell	40	7·2	0·35	0·039

Acid cell 3 was specially introduced for measurement of conductivity at very low concentrations. The area of the electrodes was greater than in the other acid cells, so as to provide a higher conductivity. It was found, however, that, when this cell was freshly introduced into a conductivity run for the purpose of measuring the last one or two solutions, values of K were obtained which were consistently lower than those secured with the other cells at higher concentrations. This was attributed to adsorption of the electrolyte on the platinum electrodes; it is conceivable that this effect should be negligible elsewhere, since, if adsorption is largely independent of the concentration of the solution, further removal of solute from solution should not occur after the electrodes have stood in the initial solution of the run. At comparatively high concentrations the effect of this adsorption must be exceedingly small, yet when a very dilute solution is involved it becomes appreciable. We therefore "inured" acid cell 3 by filling it with a solution of the appropriate acid (of roughly initial concentration) before using it on the very dilute solutions; after this treatment the cell was rinsed with water in the usual way. This process proved successful.

The stock solutions of the less soluble acids, *viz.*, *m*-bromo-, *m*-iodo-, and *p*-nitro-benzoic acids, were made up to 500 c.c. (cf. *m*- and *p*-chlorobenzoic acids, Part III), and all others to 250 c.c.

The observations made on the twelve acids are summarised in the tables, a typical run being given in each case. The water employed in making the solutions had a specific conductivity of 0·9—1·0 gemmho.

Materials.—*m*- and *p*-Toluic, *m*-bromo- and *m*-nitro-benzoic acids were purchased from British Drug Houses, Limited, *m*-iodobenzoic acid from L. Light and Co., and *p*-nitrobenzoic acid from Schering–Kahlbaum. The specimen of *m*-methoxybenzoic acid was kindly supplied by Dr. S. T. Bowden. Preliminary crystallisations were conducted with distilled water (and animal charcoal) until a steady m. p. was obtained. The *o*-iodobenzoic acid had first to be recrystallised from ether–acetone (9 : 1).

o- and *m*-Fluorobenzoic acids were prepared by the method of Dippy and Williams (J., 1934, 1466). Initial purification of the *m*-acid entailed conversion into the ethyl ester, purification of this by steam distillation, and hydrolysis with sodium hydroxide.

m-*Iodophenylacetic acid.* *m*-Iodobenzyl bromide (2 g.; 1 mol.) was heated with sodium cyanide (1 g.; 1·5 mols.) in alcohol (10 c.c.) on a water-bath for 5 hours. The oil obtained after evaporation of the alcohol was washed with water and heated with sulphuric acid (3 parts conc. acid; 2 parts water) for 20 mins. On cooling the clear liquid obtained after filtration through glass-wool, a solid separated which on recrystallisation from water (charcoal) yielded m-*iodophenylacetic acid,* m. p. 129° (Found: I, 48·0. $C_8H_7O_2I$ requires 48·5%) as colourless leaves (1 g.). *o*-Iodophenylacetic acid, m. p. 114°, was obtained (yield 40%) by a similar procedure.

We are indebted to Professor S. C. J. Olivier for the specimens of *o*- and *m*-iodobenzyl bromides.

Cell constant.	10^3 *C*.	Λ.	$10^5 K_{class.}$	$10^5 K_{therm.}$	Cell constant.	10^3 *C*.	Λ.	$10^5 K_{class.}$	$10^5 K_{therm.}$
				m-*Toluic acid.*					
0·1373	2·525	51·96	5·49	5·35	0·07236	1·098	75·80	5·49	5·37
	1·650	62·33	5·36	(5·23)		0·7696	88·47	5·46	5·36
						0·4159	114·2	5·39	5·31
		15 Determinations.		Limits of $10^5 K_{therm.}$: 5·31—5·43.					
				p-*Toluic acid.*					
0·1350	1·528	59·00	4·37	4·26	0·07236	0·5876	90·31	4·36	4·29
	1·082	68·98	4·37	4·27		0·4063	104·6	4·31	4·26
	0·7474	80·69	4·29	4·21		0·4031	105·5	4·25	4·20
		17 Determinations.		Limits of $10^5 K_{therm.}$: 4·19—4·29.					
				m-*Methoxybenzoic acid.*					
0·1373	3·619	53·13	8·26	8·00	0·07236	0·9061	99·06	8·37	8·19
	1·747	74·74	8·46	8·23		0·8245	103·0	8·36	8·19
	1·222	87·96	8·56	8·35					
		15 Determinations.		Limits of $10^5 K_{therm.}$: 8·00—8·35.					
				o-*Fluorobenzoic acid.*					
0·1367	4·124	121·3	(60·8)	(57·8)	0·07310	1·073	194·5	56·5	55·0
	1·980	156·5	56·2	54·2		0·8239	210·0	55·2	53·9
	1·385	177·5	55·8	54·0					
		10 Determinations.		Limits of $10^5 K_{therm.}$: 53·4—55·0.					
				m-*Fluorobenzoic acid.*					
0·1363	3·658	68·23	14·2$_5$	13·7	0·07316	1·046	115·3	13·6$_5$	13·3$_5$
	1·740	93·97	14·0	13·6		0·7492	133·6	14·1	13·8
	1·141	111·4	13·7	13·4		0·6205	142·7	13·8$_5$	13·5$_5$
		14 Determinations.		Limits of $10^5 K_{therm.}$: 13·3$_5$—13·9.					
				m-*Bromobenzoic acid.*					
0·1363	1·343	110·3	15·9	15·4$_5$	0·07311	0·7720	137·1	15·7	15·3$_5$
	0·9024	128·5	15·6	15·2$_5$		0·6637	145·5	15·7$_5$	15·4
						0·5438	156·8	15·7$_5$	15·4$_5$
						0·3861	177·0	15·6$_5$	15·4
		16 Determinations.		Limits of $10^5 K_{therm.}$: 15·2—15·45.					
				o-*Iodobenzoic acid.*					
0·1375	2·344	201·2	141	135·$_5$	0·07360	0·7161	275·7	139	137·$_5$
	1·195	244·2	139	136		0·4531	300·9	138	138·$_5$
	0·8688	263·9	138·$_5$	136·$_5$		0·3997	307·0	137·$_5$	138·$_5$
		14 Determinations.		Limits of $10^5 K_{therm.}$: 135·$_5$—138·$_5$.					
				m-*Iodobenzoic acid.*					
0·07236	0·3596	175·9	14·3$_5$	14·1	0·05375	0·1912	216·1	14·3	14·1$_5$
	0·2069	210·5	14·2	14·0$_5$		0·09412	261·6	14·3	14·2
						0·08389	267·3	13·9$_5$	13·9
		14 Determinations.		Limits of $10^5 K_{therm.}$: 139—142.					
				m-*Nitrobenzoic acid.*					
0·1364	3·632	100·0	33·6	32·1	0·07305	1·040	163·1	32·9	32·0
	1·945	128·7	33·1	31·9		0·7800	180·9	33·0	32·2
						0·4979	208·9	32·7	32·1
		16 Determinations.		Limits of $10^5 K_{therm.}$: 31·5—32·5.					
				p-*Nitrobenzoic acid.*					
0·1363	1·597	148·6	(39·4)	38·1	0·07319	0·7949	188·7	38·1	37·2
	1·021	173·5	38·4	37·5		0·7805	190·4	38·4	37·5
					0·05302	0·4742	221·4	(37·6)	37·0
		15 Determinations.		Limits of $10^5 K_{therm.}$: 36·9—38·1.					
				o-*Iodophenylacetic acid.*					
0·1363	1·357	87·3	9·49	9·25	0·07311	0·6795	116·4	9·40	9·21
	0·8258	107·6	9·44	9·25		0·4506	137·4	9·44	9·31
						0·2530	169·0	9·25	9·13
		19 Determinations.		Limits of $10^5 K_{therm.}$: 9·00—9·33.					
				m-*Iodophenylacetic acid.*					
0·1363	2·013	64·68	7·05	6·87	0·07311	0·4926	119·4	7·13	7·02
	1·145	83·26	7·08	6·92		0·3852	131·6	7·10	7·00
	0·7382	100·2	7·03	6·90		0·2197	162·5	7·07	6·97
		11 Determinations.		Limits of $10^5 K_{therm.}$: 6·86—7·02.					

Final purification of all acids was effected by means of conductivity water. The m. p.'s recorded below are those of the pure acids after storage; the values compare very favourably with the best in the literature.

Acid.	M. p.	M. p. (from literature).
m-Toluic	112·5°	111—113° (Auwers and Roth, *Annalen*, 1910, **373**, 245).
p-Toluic	181	181 (Ciamician and Silber, *Ber.*, 1912, **45**, 41).
m-Methoxybenzoic	110·5	110 (Ullmann and Uzbachian, *Ber.*, 1903, **36**, 1805).
o-Fluorobenzoic	127·5	124 (Cohen, J., 1911, **99**, 1063).
m-Fluorobenzoic	125	124 (Meyer and Hubner, *Monatsh.*, 1910, **31**, 934).
m-Bromobenzoic	155	155 (Holleman and de Bruyn, *Rec. trav. chim.*, 1901, **20**, 210).
o-Iodobenzoic	162·5	162 (Wachter, *Ber.*, 1893, **26**, 1744).
m-Iodobenzoic	189	187—188 (Cohen and Raper, J., 1904, **85**, 1273).
m-Nitrobenzoic	142	142 (Hubner, *Annalen*, 1884, **222**, 72).
p-Nitrobenzoic	241	240 (Fischer, *ibid.*, 1863, **127**, 137).
o-Iodophenylacetic	114·5	110 (Raum, *Ber.*, 1894, **27**, 3233).
m-Iodophenylacetic	129	

Sharp melting was observed throughout although slight softening invariably took place a few degress below the m. p. This seems to be a property of the aromatic acids studied so far; it certainly cannot be attributed to impurity.

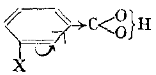
Discussion.

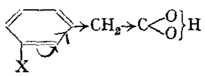
Reliable values for the thermodynamic dissociation constants in water of all the monohalogenobenzoic acids (except *p*-iodobenzoic acid, which is insufficiently soluble for measurement) are now available, and are summarised as 10^5K :

	F.	Cl.	Br.	I.
o-	54·1 †	114 *	140 *	137 †
m-	13·6₅ †	14·8 *	15·4 †	14·1 †
p-	7·22 *	10·5₅ *	10·7 *	—

* Recorded in Part III (*loc. cit.*). † Recorded in this paper.

The order Br > Cl > F for the above *o*- and *p*-series (and also for the corresponding phenylacetic acids, see Parts I and III), *i.e.*, the opposite of that to which operation of inductive effects would lead, has already been considered (Part IV; J., 1935, 346) in connexion with the data for other side-chain processes where a similar "inversion" has been observed. The whole problem has, moreover, been discussed comprehensively by Baddeley, Bennett, Glasstone, and Jones (J., **1935**, **1827**), who have provided additional data for the strengths of the halogeno-phenols and -anilines, and of certain reactions of halogeno-benzyl and -phenylethyl chlorides. Both they and Bettmann, Branch, and Yabroff (*J. Amer. Chem. Soc.*, **1934**, **56**, **1865**) have observed, in addition, irregularities in the effects of halogen substituents in the *m*-position, and our new results also make it clear that the strengths of the *m*-halogeno-benzoic and -phenylacetic acids, although not differing widely, are not in the order which would be anticipated on the basis of the inductive effects. Here again, therefore, there is some "compensating factor" decreasing in magnitude from fluorine onwards (the order first suggested by Baddeley and Bennett, J., 1933, 261); it may be suggested that this effect, whatever be its genesis, is relayed inductively from the *m*-position as follows :





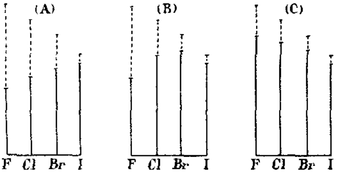
Bettmann, Branch, and Yabroff (*loc. cit.*) speak of "secondary resonance interaction" as the cause of inversion in the *m*-halogenophenylboric acids.

It was pointed out in Part IV that the effect superimposed upon the inductive effect need not of necessity cause a *complete* inversion in every instance; this is now illustrated by the fact that the iodo-acids in the *o*- and *m*-benzoic series fall out of the sequence. It is noteworthy, too, that in the *m*-substituted phenylacetic series, I < Cl. This point is

made clearer by the figure, where A, B, and C show qualitatively three possible results of the combination of the two effects; the complete lines represent acid strengths if inductive effects alone operate, and the continuous portions represent the observed strengths.

Two further points of interest emerging from the work are (i) that although, in both benzoic and phenylacetic acids, halogen leads to the greatest increase in strength when in the *o*-position, there is no abnormal effect in phenylacetic as in benzoic acid; and (ii) that the *o*- and *p*-fluoro-acids in both series are markedly weaker than the other halogeno-acids.

The dissociation constant of *m*-toluic acid may now be taken to be definitely greater than that of its *p*-isomeride; this a further example of the order of effectiveness *p*-Me > *m*-Me > H, shown also in the strengths of phenols (Boyd, J., 1915, **107**, 1540) and anilines (Flürscheim, J., 1910, **97**, 96), and in numerous side-chain reactions (*e.g.*, 15 out of 16 listed by Williams, J., 1930, **37**; compare Evans, Morgan, and Watson, J., 1935, 1178). The accurate value of $K_{therm.}$ now found for *m*-methoxybenzoic acid confirms the argument already given in Part IV (compare also the strengths of alkoxyanilines; Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469). The same remark applies to the values for *m*- and *p*-nitrobenzoic acids; further evidence is forthcoming from Williams's table of side-chain reactions (*loc. cit.*), the strengths of nitrophenols (Holleman and Herwig, *Rec. trav. chim.*, 1902, **21**, 444) and nitroanilines (Loewenherz, *Z. physikal. Chem.*, 1898, **25**, 405), and the halogenation of phenolic ethers and anilides (Jones, J., 1935, 1835). It is remarkable, however, that a *greater* relative difference is observed between *m*- and *p*-nitrophenylacetic acids (Parts I and II), and to explain this it may be suggested tentatively that hydrion arises from the methylene group of *p*-nitrophenylacetic acid, as is not impossible in view of the known reactivity of this group and the isolation of salts of suggested formula $CH(CO_2Et){:}C_6H_4{:}NO{\cdot}OM$, by Opolski and Zwislocki (*Ber.*, 1916, **49**, 1606); in this connexion, measurement of the conductivities of the esters is desirable.



(A) I>Br>Cl>F, *e.g.*, the strengths of *p*-halogenophenylacetic acids.
(B) Br>Cl>I>F, *e.g.*, the strengths of *m*-halogenobenzoic acids.
(C) F>Cl>Br>I, *e.g.*, the tautomeric mobilities of *p*-halogeno-αγ-diphenylpropenes (Shoppee, J., 1930, 968).

The relationship of the thermodynamic dissociation constants to the dipole moments of the appropriate substituted benzenes has already been pointed out (Dippy and Watson, this vol., p. 436); a similar curve is obtained, as would be anticipated, if the moments of the substituted toluenes are employed. In the plot for phenylacetic acids (Dippy and Watson, *Chem. and Ind.*, 1935, **54**, 735) the point for the *m*-iodo-acid may now be inserted; this falls further from the curve than does that of the *m*-chloro-acid.

We wish to record our indebtedness to Dr. H. B. Watson for his continued interest in this work, and to Imperial Chemical Industries, Limited, for grants.

The Technical College, Cardiff. [*Received, February 29th*, 1936.]

149. *The Slow Combustion of Formaldehyde.*

By Robert Spence.

It has been shown (*J. Amer. Chem. Soc.*, 1930, **52**, 2399, 4837; 1931, **53**, 1689; J., 1932, 686) that formaldehyde is a product of the partial oxidation of simple gaseous hydrocarbons and hydrocarbon radicals; also, it appears at an early stage in the combustion of higher hydrocarbons (cf. Ubbelohde, Drinkwater, and Egerton, *Proc. Roy. Soc.*, 1935, **153**, *A*, 103). The question has been discussed whether it plays a fundamental rôle in the chain of

reactions resulting in complete combustion, or whether it is simply a by-product. Spence and Kistiakowsky (*J. Amer. Chem. Soc.*, 1930, **52**, 4837) found that acetylene is oxidised more rapidly than formaldehyde at the same temperature (Fort and Hinshelwood, *Proc Roy. Soc.*, 1930, **129**, *A*, 284), and that the kinetic and analytical data could be reconciled to some extent by assuming that formaldehyde is essentially a by-product. Nevertheless, there remained the possibility that the supply of active centres generated thermally in the oxidation of formaldehyde may be greatly exceeded in the acetylene reaction, with the result that any formaldehyde produced would be rapidly oxidised. Recently, Steacie and MacDonald (*J. Chem. Physics*, 1936, **4**, 75), investigating the influence of additions of formaldehyde on the combustion of acetylene, found that the rate is considerably diminished thereby. These experiments show that formaldehyde is not a catalyst for the acetylene oxidation, but indicate rather that it deactivates the acetylene chain carriers. As the fate of the formaldehyde is not known, it cannot be decided whether it is itself oxidised as a result of the deactivation. However, the oxidation of formaldehyde alone has been the subject of but few investigations. Measurements by Askey (*J. Amer. Chem. Soc.*, 1930, **52**, 974) and by Fort and Hinshelwood (*loc. cit.*) show that the velocity is dependent upon a power of the formaldehyde concentration, and is practically independent of that of oxygen, the chief products being carbon monoxide and dioxide and water. The course of the reaction is clearly complex, and has now been examined analytically, further kinetic measurements being recorded.

Experimental.

Oxygen, prepared by heating A.R. potassium permanganate in a Pyrex tube, was condensed in a liquid-air trap after passing over solid potassium hydroxide and phosphoric oxide. A large first fraction was removed from the condensate, and the middle fraction collected in a 3-litre Pyrex bulb containing mercury. Formaldehyde was obtained by evaporation of the liquid monomeride (Spence and Wild, J., 1935, 338). The apparatus and quartz spiral manometer were as already described (J., 1934, 1588), but, owing to the higher temperature required for the oxidation, it was necessary to fill the electric oven with brass turnings in order to avoid a sharp temperature gradient in the interior. The gases could be separately introduced into the reaction vessel or previously mixed at 100° in a 500-ml. bulb; and temperatures were measured both by a mercury thermometer and by a thermocouple.

The Heterogeneous Reaction.—The oxidation of formaldehyde to entirely gaseous products may occur in two ways:

$$(1)\quad 2CH_2O + O_2 \longrightarrow 2H_2O + 2CO$$
$$(2)\quad CH_2O + O_2 \longrightarrow H_2O + CO_2$$

Reaction (1) is accompanied by a 50% increase in pressure, whereas (2) occurs without pressure change. It was found that in the presence of an extensive surface of powdered glass, oxidation according to reaction (2) was complete. A cylindrical reaction vessel packed with powdered Pyrex glass, previously employed (*loc. cit.*), having a volume of 32·4 ml. and a surface-volume ratio > 100, was thoroughly evacuated at 300°. Formaldehyde was admitted alone, and the fall in pressure with time noted. This was rapid at first, a decrease of 20 mm. occurring in 4 minutes, but very soon became constant at about 1 mm. per min. with 200 mm. of formaldehyde present. At this point oxygen was added. The rate of pressure decrease was at once doubled, and then fell off gradually until reaction ceased, as shown in Fig. 1. At the conclusion of an experiment, the gas mixture was drawn through a liquid-air trap by a Töpler pump, and by repeated removal of the liquid air and exhaustion, carbon dioxide could be separated from any formaldehyde, which remained in the trap in a polymerised condition. Gas analyses were performed in a simple Bone and Wheeler apparatus, the Levy tube being used for combustions. Results for two experiments are given below.

Heterogeneous oxidation of formaldehyde on Pyrex glass.

$v = 32·4$ ml.; $s/v > 100$; $T = 300°$.

	Reactants, mm.			Products, mm.				Calculated values, mm.		
No.	CH_2O.	O_2.	Δp.	O_2.	CO_2.	CO.	H_2.	CH_2O.	O_2.	Δp.
2	205·0	248·0	−92·5	36·3	191·5	11·0	7·3	202·5	227·8	11·0
3	82·0	124·0	−41·2	32·4	80·0	3·1	4·4	83·1	112·4	3·1

The hydrogen was determined by difference, but subsequent blank experiments as well as direct combustion analyses (Table I) justified the conclusion that the small amount of residual gas was hydrogen. The amount produced is about equivalent to the carbon monoxide, which indicates that these gases arise chiefly from the decomposition of formaldehyde. Consequently the carbon monoxide has not been taken into consideration in arriving at the oxygen balance. Reaction (1), therefore, does not occur to any appreciable extent in the presence of an excess of glass surface. A notable discrepancy exists between the initial oxygen figure and that calculated from the analysis. This difference of 20·2 mm. in Expt. 2 must represent condensable oxygenated products such as formic acid, which would remain in the liquid-air trap. The agreement between the initial and the calculated formaldehyde values is probably fortuitous, since considerable quantities of this gas had been adsorbed before admission of the oxygen. If it is assumed that water vapour was produced equivalent in amount to the carbon dioxide, it is clear that a small increase of pressure should have occurred. Actually, there was a considerable decrease, and it must be concluded that 90 mm. out of a total of 191·5 mm. (47%) of

FIG. 1.

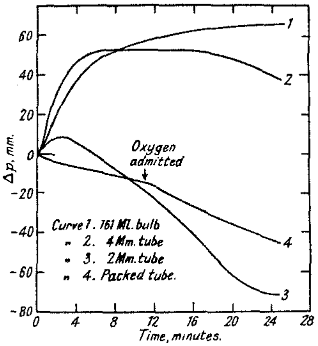
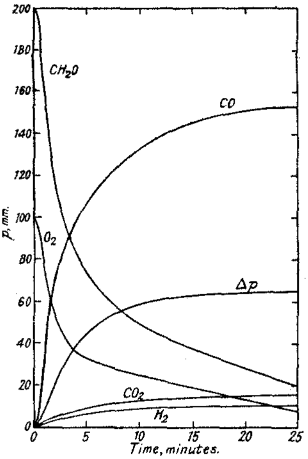


FIG. 2.



water vapour produced in Expt. 2 remained adsorbed on the wall. The corresponding figures for Expt. 3 are 42·8 mm. and 80 mm., or 53·5% adsorbed. Consideration of the pressure–time data indicates that the velocity is substantially the same when the oxygen concentration is doubled, whilst the influence of increasing formaldehyde concentration is likewise small.

Influence of Increasing Diameter.—A series of reaction vessels was prepared consisting of lengths of Pyrex tubing folded so as to diminish the bulk whilst retaining as large an internal volume as possible. However, the dead space in the spiral manometer and connecting tubing could not now be neglected, and the proper corrections were applied to the analytical results after determining the volumes and temperatures concerned. In the case of the 1-mm. tubing, the reaction vessel was connected directly to the stop-cock, and the manometer dispensed with, so only the initial pressure could be determined. Moreover, on account of the slow diffusion occurring in the narrow tubes, it was necessary to prepare the gas mixture in a 500-ml. bulb at 100° before admission to the reaction vessel. Analysis showed that approximately only 1·2 mm. of carbon monoxide, 0·18 mm. of carbon dioxide, and 0·12 mm. of hydrogen were formed at this temperature in 85 minutes. Hence any reaction occurring during the preparation of the mixture would be negligible.

TABLE I.

Influence of diameter on the velocity.

200 mm. CH_2O + 100 mm. O_2 at 317° for 25 mins.

No.	Tube.	*v*, ml.	Δp.	Products, mm. O_2.	CO_2.	CO.	H_2.	Calculated values. O_2 initial.	O_2 calc.	CO/CO_2.
56	packed	32·4	—	2·4	97·4	18·5	9·7	101·4	104·2	0·19
55	1 mm.	3·4	—	31·4	16·2	98·0	—	96·4	96·6	6·1
54	2 „	7·2	−71·5	19·4	14·2	102·3	—	100·4	84·6	7·2
52	4 „	39·0	37·3	4·2	23·2	136·5	17·9	102·4	86·7	6·0
45*h*	bulb	161·0	65·8	7·3	15·8	153·5	10·7	98·6	94·5	9·7

In this and the following tables an amount of carbon monoxide equivalent to the hydrogen produced has been subtracted before the oxygen figure (from $O_2+CO_2+\frac{1}{2}CO$) is calculated. Owing to the small volume of gas available for analysis, the whole of the oxygen supplied could not be acconnted for in every case, but it is clear that the amount of carbon monoxide produced increases steadily with the diameter, whilst the carbon dioxide drops sharply to 16 mm. in the 1-mm. vessel and then remains constant. These effects are reflected in the amount of oxygen consumed. Extraordinary pressure changes accompany reaction in the narrow vessels, as shown in Fig. 1. In Expt. 54, which is typical, there is a decrease of 71·5 mm. after an initial increase of 8·8 mm. The quantity of water produced in the reaction would account for a contraction of 65 mm. if it were totally adsorbed. Since it is unlikely that adsorption will be greater than the 53% found in the packed tube, about 30 mm. of the contraction must be due to adsorption or polymerisation of formaldehyde.

Kinetic Measurements.—The velocity of organic gaseous oxidation reactions has generally been determined from the rate of change of pressure, although complicating side reactions are always present. The principal products of the oxidation of formaldehyde in an open bulb are carbon monoxide and water. These are accompanied by smaller amounts of carbon dioxide and hydrogen, and a certain amount of polymerisation occurs at the stop-cock. The observed increase in pressure therefore represents only a fraction of the total reaction. In order to determine this relation, the products of the reaction occurring in the 161-ml. bulb have been analysed at definite intervals of time, the results being given in Table II and in Fig. 2.

TABLE II.

The progress of reaction in a single mixture.

Approx. 200 mm. CH_2O + 100 mm. O_2 in a 161-ml. bulb at 317°.

No.	*t*, mins.	Reactants, mm. CH_2O.	O_2.	Δp.	Products, mm. O_2.	CO_2.	CO.	H_2.	Calculated values. O_2.	CO/CO_2.
45*a*	0·5	199·8	98·4	1·5	89·0	—	7·8	—	92·9	—
45*b*	1·0	203·5	98·5	10·0	79·6	2·0	31·1	1·6	96·4	15·6
45*c*	1·5	196·4	98·1	15·4	61·1	3·5	54·7	3·3	90·3	15·6
45*d*	2·0	202·6	97·3	19·4	58·6	4·5	58·6	2·9	91·1	13·0
45*e*	3·0	196·8	96·2	32·4	40·7	6·7	88·5	4·8	89·3	13·2
45*f*	5·0	193·0	95·8	41·7	33·2	8·7	104·9	6·3	90·7	12·1
45*g*	8·0	196·8	98·8	55·4	27·3	12·2	125·0	8·4	97·8	10·2
45*h*	25·0	196·4	98·6	65·8	7·3	15·8	153·5	10·7	94·5	9·7

Approximately 5% of the initial oxygen is unaccounted for, and it seems probable that this may have been lost in the form of condensable products such as formic acid. The relation between ΔCH_2O and Δp is approximately linear in the early stages of the reaction, and if it be assumed that the same relation holds for other mixtures, different rates of reaction can be determined by measurement of the rate of pressure change. Gas analyses of six different mixtures suggest that the assumption is legitimate. The mean value of $\Delta CH_2O/\Delta p$ obtained from Fig. 2, is approximately 3 up to 50% of reaction and then diminishes to about 2·7.

The quantitative value of the kinetic data is unfortunately adversely affected by a slow increase in the activity of the surface, although it is only in fast reactions that serious differences appear, and some approach to an average has been obtained by suitable ordering of the experiments. Wide variations in the concentration of oxygen have little influence on the rate (Table IIIa), whereas an increase in the formaldehyde concentration is accompanied by an

TABLE III.

(a) *Influence of oxygen concentration on the initial rate.*

200 mm. CH_2O; v = 161 ml.; T = 317°.

No.	11	10	12	13	9	7	17
O_2, mm.	14·1	25·5	29·0	53·5	57·6	102·1	288·5
dp/dt	5·5	6·5	6·5	6·8	5·8	6·0	7·0

(b) *Influence of formaldehyde concentration on the initial rate.*

200 mm. O_2; v = 161 ml.; T = 317°.

No.	CH_2O, mm.	dp/dt.	dp/dt, calc.*	No.	CH_2O, mm.	dp/dt.	dp/dt, calc.*	No.	CH_2O, mm.	dp/dt.	dp/dt, calc.*
22	39	0·02	0·04	25	116·5	2·5	2·4	28	223	15·0	13·2
26	90	1·0	1·0	20	128·7	2·5	3·2	29	263	29·0	19·6
21	109	2·0	1·9	24	190	8·0	8·9	18	333	31·0	33·4

* For equation upon which calculated values are based, see p. 655.

important increase in the velocity (Table IIIb); dp/dt is given in mm. per min., and for Expt. 22, the value has been calculated from analytical data. Fort and Hinshelwood (*loc. cit.*) have calculated an energy of activation of 20,000 cals. from determinations of the time of half-reaction at different temperatures. It is questionable, however, whether such values form the most satisfactory basis for the calculation, since the velocity of a single reaction does not always decrease according to the initial rate law. For this reason, the initial rates have been measured over a similar range of temperature, and the apparent energy of activation calculated. After

Dependence of initial velocity on temperature.

200 mm. CH_2O + 100 mm. O_2; v = 161 ml.

Nos.	T.	dp/dt.	No.	T.	dp/dt.
35, 37	277°	5·0	32	327°	13·0
33, 34	297	8·0	36	337	18·5

correction for the change in formaldehyde concentration in each case, this gives a value of 17,600 cals. According to Askey (*loc. cit.*), increase of temperature results in an increase in the proportion of carbon dioxide in the products. Analysis of the same mixture at 277° and at 337° gave CO/CO_2 ratios of 5·5 and 8·5 respectively, but this result does not appear to be in serious contradiction to Askey's experimental data since the reduction in the final pressure increase upon which his conclusion is based occurs above 346°.

DISCUSSION.

It is important, first, to decide whether the reaction is simple or of the chain type. The influence of diameter is always a useful criterion in this connexion, and it can be seen from Table I that an increase in diameter is accompanied by an increase in the rate of formation of carbon monoxide. The existence of an induction period and the complex reaction kinetics observed are also in accord with the idea of a chain mechanism. It is, nevertheless, surprising that the production of carbon monoxide, which presumably occurs homogeneously, should still be quite rapid in vessels of 1 mm. diameter, and it might be alleged that the apparent diminution in velocity is entirely due to the removal of formaldehyde by polymerisation or adsorption. However, the amount of oxygen reacting in the 4-mm. tube is approximately equal to that in the open bulb, and it seems probable that the inhibition of reaction (1) is real. In the packed tube, the amount of carbon monoxide arising from oxidation is very small, although pressure–time measurements indicate that the homogeneous reaction in an open bulb at this temperature is the faster. Inhibition of the homogeneous reaction appears to occur, therefore, at some diameter less than 1 mm., and it may be confidently assumed that the oxidation of formaldehyde in open vessels is a chain reaction. Considered from the point of view of Semenoff's theories ("Chain Reactions and Chemical Kinetics," 1935, pp. 344—376), the form of the Δp–time curve and the general kinetic properties place the reaction in the acetylene–aldehyde class of oxidations. Indeed, Semenoff's predictions with regard to this type of reaction have to a certain extent been fulfilled, *viz.*, that the velocity in a single experiment may remain approximately constant

for a considerable fraction of the reaction or decrease more slowly than would be expected from the initial rate law, and that the velocity–time curve should be initially concave. In certain of the most rapid reactions studied, the velocity was constant or nearly so until some 60% of the formaldehyde had disappeared. In most of the cases shown in Table IV, however, the rate adheres more closely to the theoretical. The rate–time curve deduced from the analytical data for the production of carbon monoxide is slightly but definitely concave, and it seems improbable that this concavity can be due to the slow heating of the gas mixture, which is prepared at 100° and passes into the vessel *via* capillary tubing at 317°. If anything, the carbon monoxide figure for $\frac{1}{2}$ minute is too large, since the gas cannot be wholly removed upon opening the stop-cock but is reduced first of all to a pressure of a few cm. and then slowly pumped out by the Töpler pump. Semenoff has shown that the velocity of oxidation of a saturated hydrocarbon increases with time according to the equation $\log \Delta p = \text{const.} + \psi_0 t$. If we consider Expt. 47, in which the increase of velocity with time can be noticed, and plot $\log \Delta p$ against t as in Fig. 3, only

Fig. 3.

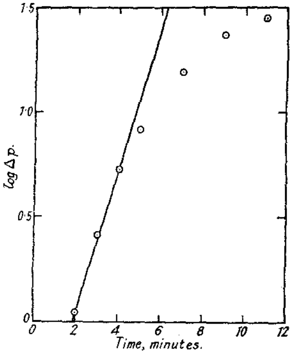
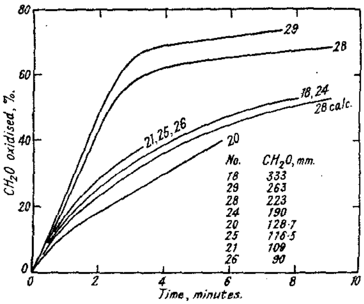


Fig. 4.



the first few points lie on a straight line. In the oxidation of formaldehyde, therefore, the maximum rate is attained at a comparatively early stage, and not when only half of the

Expt. 47; 200 mm. CH_2O + 100 mm. O_2; $T = 277°$.

t, mins.	2	3	4	5	7	9	11
Δp	1·1	2·6	5·3	8·2	15·6	23·4	28·2
$\log \Delta p$	0·0414	0·4150	0·7234	0·9139	1·1931	1·3692	1·4502

organic reactant remains, as in the case of saturated hydrocarbons. From the linear portion of the curve we have $\psi_{0\,\text{min.}} = 0{\cdot}34$, and since $\phi_0 = 2{\cdot}3\psi_0$ (Semenoff, *ibid.*), $\phi_{0\,\text{sec.}} = 0{\cdot}013$. This compares with the value 0·04 obtained for acetylene at 320°, which was unfortunately given as 0·4 in the previous paper (Spence, *loc. cit.*). According to Semenoff's view, reactions of this type are characterised by an interaction between the chains. The larger the supply of initial centres, the greater the chance of interaction, with the result that the induction period would become shorter, and the velocity would tend to maintain its initial value for a longer period. Bäckström (*Z. physikal. Chem.* 1934, *B*, **25**, 99) has proposed a chain mechanism for the oxidation of aldehydes which accounts very well for the liquid-phase oxidation, and it seems probable that a similar mechanism involving interacting, branched chains might prove satisfactory in this case. Direct adaptation of Bäckström's scheme would lead to a highly complicated series of

reactions, but it has been possible to devise the following mechanism by supposing that at 320° the activated aldehyde will react rapidly with oxygen, giving an unstable complex.

(1) $$O_2 + \mathrm{H{\cdot}\underset{O^-}{C}H^-} \longrightarrow \mathrm{H{\cdot}CHO_3}$$

(2) $$\mathrm{H{\cdot}CHO_3} \longrightarrow \mathrm{H{\cdot}\underset{O^-}{C}H^-} + O_2$$

(3) $$\mathrm{H{\cdot}CHO_3} + \mathrm{H{\cdot}CHO} \longrightarrow 2\mathrm{H{\cdot}\underset{O^-}{C}(OH)^-}$$

(4) $$\mathrm{H{\cdot}\underset{O^-}{C}(OH)^-} + \mathrm{H{\cdot}CHO} \longrightarrow H_2O + CO + \mathrm{H{\cdot}\underset{O^-}{C}H^-}$$

(5) $$\mathrm{H{\cdot}CHO_3} + \mathrm{H{\cdot}\underset{O^-}{C}(OH)^-} \longrightarrow CO_2 + CO' + 2H_2O$$

(6) $$CO' + \mathrm{H{\cdot}CHO} \longrightarrow \mathrm{H{\cdot}\underset{O^-}{C}H^-} + CO$$

(7) $$\mathrm{H{\cdot}\underset{O^-}{C}(OH)^-} \longrightarrow \begin{cases} \mathrm{H{\cdot}CO_2H} \\ H_2O + CO \\ H_2 + CO_2 \end{cases}$$

Branching occurs by the formation of two activated formic acid molecules by reaction (3), whilst the chain interaction (5) counteracts the chain-breaking process (7) so that the reaction, once started, will continue until the cycle breaks down. It is assumed that activated formic acid is concerned in the chain, otherwise this substance might be expected to become an important end-product. Formaldehyde is activated according to reaction (6) by collision with an excited carbon monoxide molecule, but excited carbon dioxide or water could equally well be represented as the activating agent. After collection of constants, the following parabolic equation is obtained :

$$-\,d[CH_2O]/dt = k'[CH_2O]^2 - k''[CH_2O] + k'''$$

where $k' = 3k_3k_4/k_5$, $k'' = 4k_3k_7/k_5$, and $k''' = k_3k_7^2/k_4k_5$. When empirical values calculated from the initial-rate measurements given in Table IIIb are substituted, we have

$$-\,d[CH_2O]/dt = 1{\cdot}17 \times 10^{-4}[CH_2O]^2 - 9{\cdot}21 \times 10^{-2}[CH_2O] + 1{\cdot}9395$$

and the initial rates obtained from this equation are compared with those obtained experimentally in Table IIIb. The value of the constant term is slightly greater than that expected from the theoretical relations between k', k'', and k''', and it is conceivable that another term should be included representing the initial supply of active centres. The ratio k_4/k_7, calculated from the empirical values of k' and k'', is about 1/50, *i.e.*, the activated formic acid is relatively easily decomposed or deactivated. It would appear also that k_5 is large, so that chain interaction occurs readily. In the above equation, $-\,d[CH_2O]/dt$ is a minimum at $[CH_2O] = 39{\cdot}4$ mm., but owing to the lack of experimental data in this region, no attempt has been made to remedy this. Moreover, it is doubtful whether the Bodenstein method of derivation of a velocity expression is strictly applicable in this case, since stationary concentrations of intermediates are probably not attained. However, we can attempt to calculate the course of a single experiment from the integrated form of the velocity equation :

$$t = 81{\cdot}55 \tan^{-1}x/[9{\cdot}545 \times 10^{-2}a(a - x) - 3{\cdot}755(2a - x) + 158{\cdot}1]$$

where a is the initial pressure of formaldehyde, and x the decrease in formaldehyde pressure after t minutes. Curves have been plotted for each initial pressure and the percentage reaction after given intervals of time obtained. These values are compared with the experimental data in Table IV. Where more than 50% of reaction has occurred, the factor $\Delta[CH_2O]/\Delta p$ for the particular pressure increase concerned has been deduced from Fig. 2.

TABLE IV.

The experimental and the calculated course of reaction in different mixtures.

O_2 = 100 mm.; v = 161 ml.; T = 317°.

CH_2O, 333 mm.			CH_2O, 263 mm.			CH_2O, 223 mm.			CH_2O, 190 mm.		
t.	%, obs.	%, calc.	*t.*	%, obs.	%, calc.	*t.*	%, obs.	%, calc.	*t.*	%, obs.	%, calc.
0·5	14·4	13·2	0·2	6·8	4·6	0·2	4·0	3·6	2	22·2	20·4
1	25·2	22·5	1	33·0	17·7	1	20·7	14·6	4	35·1	32·8
2	38·7	36·0	2	63·3	29·1	2	44·4	23·2	6	42·6	39·0
3	47·0	44·8	4	70·8	42·4	5	64·0	41·2	10	52·1	49·6
4	52·9	50·5	6	73·5	49·1	11	69·0	55·8			

CH_2O, 128·7 mm.			CH_2O, 116·5 mm.			CH_2O, 109 mm.			CH_2O, 90 mm.		
1	5·8	6·8	1	6·4	5·7	2	10·5	9·2	2	6·7	6·1
4	16·3	20·5	2	12·9	10·3	4	19·0	16·1	4	13·7	11·1
8	25·6	32·4	4	21·9	17·8	8	31·1	25·7	8	23·7	19·1
16	39·9	44·8	8	35·8	28·3	12	37·7	32·2	12	30·0	24·7

The theoretical curve for Expt. 28 (CH_2O, 223 mm.) has been plotted in Fig. 4, and the experimental curves constructed on this as a base line. Six experimental curves representing formaldehyde pressures ranging from 90 to 333 mm. lie quite close to the theoretical, whilst in two cases the initial velocity remains unchanged until about 50% of the formaldehyde has reacted. This effect can scarcely be due to overheating of the gas, since it does not occur in every instance, even at high initial rates; nor can it be due to some abnormal reaction, for the usual products appear in the usual ratios. In, *e.g.*, Expt. 29, 263 mm. CH_2O + 100 mm. O_2 gave 22·5 mm. CO_2, 162·0 mm. CO, and 16·8 mm. H_2 in 10 minutes, whilst only 2·8 mm. of O_2 remained. The pressure should have increased by 89·4 mm. whereas an increase of 73 mm. was recorded, the difference presumably being due to polymerisation. There was no further pressure increase after 6 minutes, and the percentage reaction calculated from Δp in the manner described previously was 73·5, in good agreement with the analytical results, which correspond to 70% of reaction. Although the tendency towards a lower order of reaction appears to depend to some extent on the initial velocity, this is clearly not the only factor. The effect is most pronounced in experiments occurring later in the series, when the surface is most active, and it seems reasonable to conclude that the state of the surface is of great importance in this connexion. Perhaps the chains branch on a surface which is in a suitable state of activity, but it will be necessary to obtain fnrther results before any definite conclusions can be drawn.

It is important, if the combustion mechanism is to be complete, to take account of the carbon dioxide and the hydrogen which are produced. Consideration of Table II shows that the carbon dioxide formed in an open bulb at 317° cannot wholly originate from the purely heterogeneous reaction, since there is no direct proportionality between the extent of surface and the concentration of carbon dioxide. It is supposed, in the mechanism, that hydrogen and carbon dioxide are produced by one of three possible deactivations or decompositions of the activated formic acid. Hydrogen may also arise from the decomposition of formaldehyde itself. Thus, concentrations of carbon monoxide and of hydrogen of the order of 0·5 mm. are produced from 200 mm. of formaldehyde at 317° in 10 minutes. It is possible that this decomposition is accelerated by oxygen, but in view of the close parallelism between the amounts of hydrogen and of carbon dioxide produced in the oxidation (cf. Table II), decomposition of the activated formic acid seems to be the more likely source of the hydrogen. The fact that the ratio CO/CO_2 decreases during the course of a single experiment points to the same conclusion, since reaction (4) should occur less frequently as the formaldehyde is consumed, whilst (5) and particularly (7) should become relatively more important. As regards the heterogeneous reaction, little further can be said. Davies (*Phil. Mag.*, 1936, **21**, 513; and unpublished results) has found that under suitable conditions of concentration and temperature, the combustion of methane on a platinum wire is complete, but when carbon monoxide is adsorbed on the wire, the reaction is inhibited. Now, if the production of normal carbon monoxide were an important stage in the oxidation, rapid self-poisoning should take place. The fact that this does not occur

indicates that carbon dioxide must be produced directly or through the nascent or active carbon monoxide of the type postulated in the foregoing mechanism. Some experiments recently carried out in collaboration with Dr. Davies, and shortly to be published, indicate that similar considerations apply in the case of formaldehyde.

SUMMARY.

Formaldehyde reacts rapidly with oxygen in Pyrex glass vessels at 317°. In unpacked vessels, of diameters ranging from 1 mm. upwards, the chief products are carbon monoxide and water, whilst in a vessel packed with powdered glass, combustion to carbon dioxide and water is complete.

The kinetics of the reaction have been studied, and a chain mechanism has been proposed which partly accounts for the results.

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THE UNIVERSITY, LEEDS. [*Received, February 19th, 1936.*]

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150. *The Thermal Decomposition of Sodium and Potassium Azides.*

By W. E. GARNER and D. J. B. MARKE.

THE alkaline-earth azides possess activation energies in the neighbourhood of 20 kg.-cals., whereas for lead azide, this energy is 38 kg.-cals. for the α-form, and 37 kg.-cals. for the β-form (see later). The alkali azides have not been investigated from this point of view, and one of the objects of the present investigation is to fill this gap in our knowledge.

According to earlier investigations, the decomposition of the alkali azides begins to be appreciable at temperatures 30—40° below the melting points of the salts, *i.e.*, at 260—320°, whereas the more sensitive azides of the alkaline-earth metals decompose at temperatures in the neighbourhood of 100° (Tiede, *Ber.*, 1916, **49**, 1742; Andreew, *Physikal. Z. Sowjet-Union*, 1934, **6**, 121; Harvey, *Trans. Faraday Soc.*, 1933, **29**, 653). Lead azide, on the other hand, which is much more sensitive than the azides of the alkaline earths, decomposes at appreciable rates only at temperatures above 220° (Garner and Gomm, J., 1931, 2129). Since the activation energy is usually greater the higher the temperatures at which the reactions take place, it appeared likely that the activation energies of the alkali azides would be higher than those of any of the azides hitherto studied; this has not been found to be the case, although the values, 36·1 and 34·4 kg.-cals. for the potassium and the sodium salt respectively, are much higher than those of the azides of the alkaline earths. The cause of the discrepancy is shown to lie in the high volatility of the metallic products of the alkali azides, which reduces the area of the interface at which the reaction can proceed, and thereby increases the temperature at which reaction can first be observed.

A further point of interest in the study of the alkali azides concerns the nature of the nuclei from which the reaction spreads. The decomposition of solids normally commences at nuclei which increase in number and size as the reaction proceeds. In the majority of solid reactions there is an induction period followed by a reaction at an accelerating rate. The induction period, certainly in the case of hydrates and probably also in the case of other solids, is mainly due to the very slow rate of growth of the nuclei when first formed (Bright and Garner, J., 1934, 1872; Garner, Gomm, and Hailes, J., 1933, 1393; Garner and Southon, J., 1935, 1705). The causes of the slow rate of growth of small nuclei are still obscure, but one of the authors, on the basis of the fact that rate of evolution of gas in many cases is given by dp/dt = const. e^{kt}, has concluded that the nuclei grow by means of a branching-chain mechanism. For potassium azide, experimental evidence is brought forward which shows that in the neighbourhood of 330° the reaction spreads into the mass of the crystal at an accelerating rate and possesses the characteristics of a chain reaction.

EXPERIMENTAL.

Preparation of Sodium and Potassium Azide Crystals.—Two specimens of sodium azide, from Schuchardt's and from British Drug Houses, were employed. Schuchardt's potassium

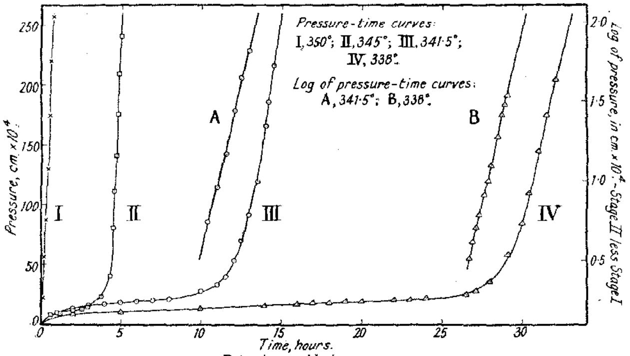
azide was used. Purification was effected by dissolving the crystals in water to give saturated solutions. After filtration, an equal volume of alcohol was added and the precipitated azide was washed with alcohol and dried in a vacuum desiccator (cf. Briner and Winkler, *J. Chim. physique*, 1923, **20**, 206). The azides were then redissolved in water, and crystals obtained by slow evaporation at room temperature. The solutions were rejected after they had stood for 5 or 6 days, as it was considered probable that hydrolysis of the azide and the evaporation of hydrazoic acid would interfere with the quality of the crystals.

Potassium azide. The crystals were well-formed tetrahedra except for one face, the under side of the crystals, where a deep crater occurred. These crystals were free from chloride, and analysis by conversion into silver azide and weighing the silver as chloride gave their purity as 99·5, 100·1%.

Sodium azide. This salt could not be obtained as single crystals but as star-shaped aggregates 1—2 mm. in length. It was analysed by the above method and shown to contain the theoretical quantity of azide (99·8, 100·9%).

Decomposition of Crystals of Potassium Azide in a Vacuum.—Measurements of the rates of decomposition were carried out in an apparatus of the type described previously (Garner and

Fig. 1.



Potassium azide in a vacuum.

Hailes, *Proc. Roy. Soc.*, 1933, *A*, **139**, 576). A single crystal, 1—3 mg., was employed, and this was lowered into the evacuated reaction vessel in a small platinum bucket. The course of the reaction was followed on a McLeod gauge by measurements of the nitrogen liberated. The m. p. of potassium azide is about 350° and it was not found possible to study the rate of decomposition below 330°. The typical pressure–time curves in Fig. 1 show that when the azide is solid, there is an initial evolution of gas, the rate of which slowly decreases to an approximately constant value. After a period of time which increases as the temperature is lowered, the reaction commences to accelerate, the acceleration obeying the same relationship as found previously for mercury fulminate, lead azide, barium azide, and lead styphnate, *viz.*, dp/dt = const. e^{kt} (Fig. 1, A and B). The rate of this reaction varies as the 10th to the 30th power of the time. The solid reaction thus takes place in two stages, and in this respect potassium azide resembles mercury fulminate, although for the latter the initial surface reaction is less prominent. Above the m. p., the rate of reaction is very rapid and resembles in character the second stage of the solid reaction (Fig. 1).

Microscopical examination of the crystals after various periods of heating has thrown light on the two stages of the reaction. During stage I, the crystals become rounded at the edges, and the surface becomes eroded along lines which may have been originally cracks. The crystals remain colourless, and since the potassium produced by the decomposition volatilises away, no nuclei can be observed on the surface. The reaction is obviously occurring mainly along the

edges of the crystal and may be due to incipient melting or loosening of the lattice along these edges. The rate of this stage of the reaction is not much affected by temperature.

Stage II is accompanied by marked changes in the appearance of the crystal: it becomes divided into rounded blocks some of which are blue and others colourless. Holes of the approximate size of a block appear in the crystal, which soon has the appearance of a honeycomb. This stage of the reaction is apparently a process which is disseminated throughout isolated portions of the crystal lattice, and is accompanied by the liberation of potassium metal in a finely divided state. The process must start from nuclei, since it is limited to individual blocks of the crystal. The reaction being of the accelerating type, the infected blocks decompose rapidly, giving rise to the honey-comb structure.

The degree of reproducibility of the rate of reaction from one crystal to another is poor, and also irregularities occur which make it impossible to determine the temperature coefficients for

Fig. 2.

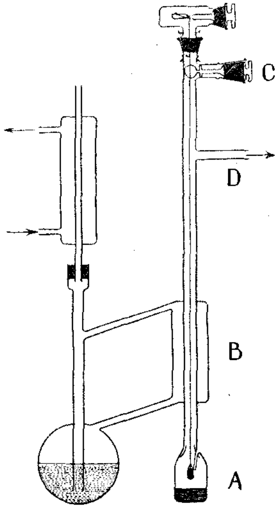
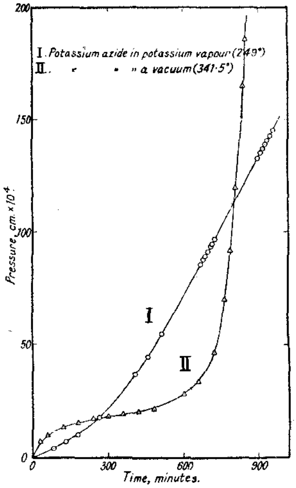


Fig. 3.



either stage I or stage II. In the case of solid reactions, there is always found some variation in the rate of reaction from crystal to crystal due to minute differences in crystal structure, but potassium azide shows much greater irregularities than usual. These it was thought might be due to variations in the rate at which potassium metal evaporated from the surface, so it was decided to study the decomposition in the presence of a constant vapour pressure of potassium.

Decomposition of Potassium Azide in Potassium Vapour.—After many attempts a suitable type of apparatus was designed (Fig. 2). The reaction vessel consists of a cylindrical Pyrex bulb *A*, into which is fused a glass tube to take the thermocouple junction. After a thorough baking-out of the apparatus, potassium, carefully freed from paraffin, is distilled into *A*. This metal can be vaporised by surrounding the reaction vessel with an electric furnace at the required temperature, and condensed by means of the condenser *B*, which is attached to a boiler containing a non-inflammable liquid of which the b.p. is above the m. p. of the metal. Glass flanges at the top of the reaction vessel direct the condensed potassium away from the centre of the reaction vessel where the crystal is suspended. The inner tube of the condenser is extended up to a circular glass stop at *C* which can be rotated by a ground joint. This extension serves

as an air condenser, and the glass stop prevents any potassium atoms not condensed below from reaching the ground joints at the top of the apparatus. The crystal was lowered into the reaction vessel in a heavy platinum bucket by means of a thin platinum wire attached to the spindle device previously described. The wire is corroded by the potassium vapour and has to be frequently renewed. The pumps were connected at D through a liquid-air trap.

The potassium interacts with the water in the glass at 200—300° and gas is given off in considerable quantities, so it was necessary to bake out for 1—3 weeks before introducing a crystal. After being baked out, the apparatus is filled with dry nitrogen, and the crystal introduced at the top of the apparatus. After re-evacuation, the crystal is lowered into the potassium vapour in the reaction vessel, and measurements of the pressure started immediately.

In potassium vapour, the decomposition could be followed down to 220°, which is 100° lower than the lowest temperatures at which observations could be made in a vacuum. The form of the pressure–time curve is radically different from that obtained in a vacuum: those obtained

FIG. 4.

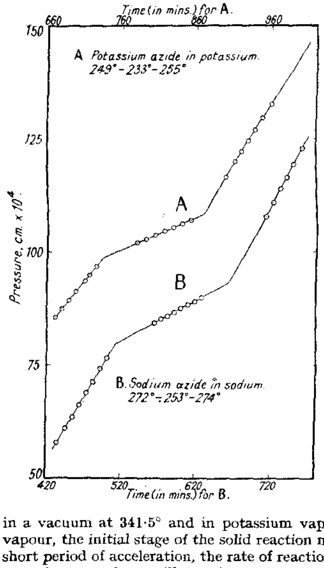
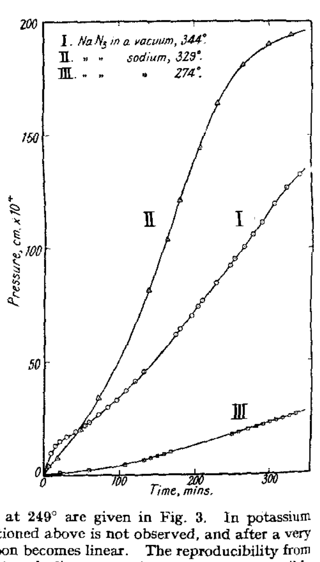


FIG. 5.



in a vacuum at 341·5° and in potassium vapour at 249° are given in Fig. 3. In potassium vapour, the initial stage of the solid reaction mentioned above is not observed, and after a very short period of acceleration, the rate of reaction soon becomes linear. The reproducibility from crystal to crystal was still unsatisfactory, however, but the linear rate of reaction made it possible to determine the activation energy with one crystal (see later). Examination of a partly decomposed crystal showed that the reaction was occurring mainly on the external surface, and that the honey-comb structure was not formed to any appreciable extent. Observation of the surface is, however, difficult on account of the presence of the metal, which rapidly oxidises in the air.

The Activation Energy of Potassium Azide.—A crystal of the azide was heated until it gave a constant rate of evolution of gas, and then the temperature of the furnace was lowered by about 20° and further readings taken. The temperature was then raised to its original value and the rate again measured (Fig. 4, A). If the rate of evolution of gas was unaffected by the double change of temperature and remained linear throughout, the experiment was considered satis-

factory. It is important that the crystals be not subjected to too great or too sudden a change in temperature, otherwise the rate of reaction on return to the original temperature may be increased, probably owing to an increase of the surface due to cracking. It is rare that more than one experiment can be carried out with one filling of potassium, on account of the breaking of the suspension wire on attempts to remove the crystal. The results are summarised in Table I, where E represents the activation energy. The rates in col. 4 are given as the number of molecules of nitrogen evolved for unit area of the crystal in one second. The areas of a number of crystals were measured and found on an average to give an external area of 0·141 cm.^{2} for 4·5 mg.

TABLE I.

Activation Energy of Potassium Azide in Potassium Vapour.

Expt.	Wt., mg.	Temp.	Rate $\times 10^{-15}$.	E, kg.-cals.	Expt.	Wt., mg.	Temp.	Rate $\times 10^{-15}$.	E, kg.-cals.
7	2·8	243·6°	1·02	33·1	10	5·45	250·8°	1·74	36·2
		224·6	0·30				230·4	0·43	
8	5·2	247·9	4·55	35·6	11	4·45	249·0	1·23	36·4
		221·7	0·75				233·1	0·41	
		238·3	2·76	39·8			255·0	1·57	32·8

In Expts. 7 and 10, the second stage of the experiment was unsatisfactory since the reaction was no longer linear. The greatest weight is placed on the first values of Expts. 8, 10, and 11, and these give a mean of 36·1 kg.-cals. The calculated rate of condensation of potassium on the surface of the azide is more than 1000 times greater than the rate of reaction, being $7·2 \times 10^{18}$ atoms/cm.^{2}/sec. at 222°.

The Decomposition of Sodium Azide.—The m. p. lies above 365° according to our measurements, and it was possible to follow the solid reaction from this temperature down to 257°. In a vacuum, the pressure–time curves are similar to those of the potassium salt in potassium vapour, except that an initial surface reaction is present to a very slight extent. The acceleration of the rate commences very soon after the insertion of the crystal, but it soon disappears in a practically linear rate of reaction. A partly decomposed crystal shows a block structure, but the honey-comb is only slightly developed. Some of the blocks are coloured pink instead of blue, as observed with potassium azide. A typical curve for sodium azide in a vacuum at 344° is shown in Fig. 5, together with curves for the azide in sodium vapour at 329° and 274°. The catalytic effect of sodium vapour is much smaller than that of potassium on potassium azide.

Activation Energy of Sodium Azide.—This was obtained by measurements in sodium vapour as previously described for potassium. Special care has to be taken in purifying the sodium, otherwise faulty results may be obtained. This, we consider, is due to the coating of the surface of the azide with the impurities present. The results are collected together in Table II, and a typical pressure–time curve is given in Fig. 4, B. The rates of decomposition are calculated and expressed as before. The crystals of sodium azide were much more irregular in shape than those for the potassium salt, and hence the rates in col. 4 will be maximum values.

TABLE II.

Activation Energy of Sodium Azide in Sodium Vapour.

Expt.	Wt., mg.	Temp.	Rate $\times 10^{-15}$.	E, kg.-cals.	Expt.	Wt., mg.	Temp.	Rate $\times 10^{-15}$.	E, kg.-cals.
6	4·45	271·9°	1·71	35·0	9	4·8	273·9°	(3·69)	(27·9)
		252·6	0·525				241·6	0·75	33·6
		273·6	1·81	33·9			260·8	2·42	32·4
7	4·75	268·3	0·99	35·8			240·6	0·73	33·2
		247·6	0·265				260·6	2·46	
		264·3	0·77	35·7					

The rate of collision of sodium atoms per second with 1 cm.^{2} of surface is $1·31 \times 10^{18}$ at 272° and $0·58 \times 10^{18}$ at 253°, and these rates are approximately 1000 times greater than the rates of reaction. Thus the surface of the crystals is probably completely covered with sodium during the reaction. The average activation energy for the range 240—275° is 34·4 kg.-cals.

Residue after Decomposition.—With both azides, particularly the sodium salt, it was difficult to carry the decomposition through to the end, and with sodium azide in a vacuum at 348°, the reaction almost reached a standstill when only 85% of the gas had been given off. Analysis of

the white amorphous residue with silver nitrate showed that it was not hydroxide but possessed the properties of an azide, giving a white precipitate soluble in nitric acid. On heating to 361° in vacuum, sodium azide was decomposed to the extent of 92%, but it was only when the azide was heated in the metallic vapour at 329° that complete decomposition could be brought about. Even in this case, the final stages of the reaction were always slow. Since the analyses showed that there could be only a small amount of impurity present, it is concluded that the retardation of the rate of evolution of gas which occurs at the end of the experiment is due to the coating of the crystal blocks with a layer of non-volatile impurity. A very small amount of impurity would be sufficient to account for the results. This effect of impurity is very marked in the case of the alkali-metal azides, since the whole of the products are volatile.

Discussion.

Potassium and sodium azide crystals undergo appreciable decomposition at temperatures above 330° and 270° respectively, to give the metal and nitrogen. On account of the volatility of the metal, there is no permanent interface between the salt and its products; and the reaction occurs partly on the external surface of the crystal and partly in the interior. The surface reaction is rapid at first and then falls off to a steady rate. The internal process possesses an induction period which is very marked in the case of potassium azide and decreases with increase in temperature. The internal reaction proceeds stepwise from one fragment of the crystal to another, and the blocks become penetrated by the metal, and the disappearance of some of them gives rise to the honey-comb structure. The phenomena are of such a coarse texture that ' bumps ' sometimes appear on the pressure–time curves. The relation $dp/dt =$ const. e^{kt} is, however, obeyed within the experimental error. The process occurring within the solid is so complex that it is difficult to decide whether the rate-determining process is the spread of reaction chains throughout the individual grains or is due to a chain-like propagation of the reaction throughout the blocks. Either process would account for the acceleration of the reaction.

The rate of decomposition of the alkali azides in the presence of the saturated vapour o the metal is greater than in a vacuum : for the potassium salt the rate of reaction at 240 in the metal vapour is approximately the same as that in a vacuum at 340°. In the presenc of the saturated metallic vapour, the azide surface will be covered with a metallic filr possibly many atoms thick, and since the rate of condensation of potassium from th vapour phase is 1000 times greater than the rate of liberation of potassium by the chemica reaction, this film of potassium atoms will be maintained practically intact throughou the reaction. The reaction at the lower temperatures occurs mainly in the neighbourhoo of the interface between the azide and the metal, and the reaction in the interface is thus th most rapid process occurring, as is usually observed with solid reactions. The only excep tion so far known is the decomposition of " nitrogen iodide " (NI_3,NH_3), where the reactic is retarded by the products (Garner and Latchem, *Trans. Faraday Soc.*, 1936, **32**, 567 Sodium vapour accelerates the decomposition of sodium azide, but since the volatility sodium is less than that of potassium, the interface in a vacuum possesses greater stabilit and the acceleration is not so marked.

The Activation Energies of the Azides.—Since the activation energies found for sodiu and potassium azide are derived from the temperature coefficient of the surface reacti occurring at the interface between the azide and the metal, they can be directly compar with the energies derived for lead, calcium, and barium azides, where the metal is practica non-volatile at the temperature of the experiment. The experimental values for the and β-lead azides have been re-examined in order to decide upon the accuracy of the resu previously quoted for the activation energies.

α-Lead Azide.—There are three values for each range of temperature and these ha been averaged and the activation energies calculated for each range.

Temp.	220—230°	230—240°	240—250°	250—260°	260—270°	270—28
E, kg.-cals.	37·9	38·1	39·3	37·8	54·4	70·3

It is evident that *E* is rapidly rising above 260°, and only below this temperature is approximately constant. The average value between 220° and 260° is 38 kg.-cals.

β-*Lead Azide.*—Only four experiments were made :

Temp.	200—210°	210—220°	250—260°	260—270°
E, kg.-cals.	29·1	34·0	49·7	36·2

The average is 37 kg.-cals. and is very approximate since individual values are so discrepant.

Calcium Azide.—Andreew (*loc. cit.*) showed that this substance gave a strongly accelerating reaction and that the activation energy increased with temperature.

Temp.	60—80°	80—100°	93—105°	120—130°
E, kg.-cals.	21	22	27	30

Barium Azide.—Harvey (*loc. cit.*) found that *E*, calculated from the acceleration constant of the reaction, showed no signs of increase between 100° and 130°, remaining constant at 21 kg.-cals.

The azides are arranged below in the order of increasing sensitivity :

Substance	NaN_3	KN_3	BaN_6	CaN_6	α-PbN_6	β-PbN_6
Range of temp.	240—275°	222—255°	100—130°	60—130°	220—260°	200—270°
E, kg.-cals.	34·4	36·1	21	20—30	38	(37)

It will be observed that the activation energies are of the same order as those of gaseous reactions at similar temperatures, and that the activation energy is the greater the higher the temperature at which the solid reaction first becomes measurable. There is no direct relationship between sensitivity and activation energy, the sensitive lead azide decomposing over the same temperature range as and with a similar activation energy to those found for the inert alkali azides. The azides of the alkaline earths, with an intermediate sensitivity, possess much smaller activation energies. Andreew has shown that nitrides are produced as intermediate compounds from calcium and barium azides, so it is possible that the mechanism of the reaction in these cases is not the same as for the lead and the alkali azides, where the metal and nitrogen are produced directly. It may be that in the azides of the alkaline earths only one N_3 ion is activated at a time, whereas in the other azides the ions are activated in pairs.

For the experiments on lead and potassium azides, the area of the interface is known approximately, and hence it is possible to calculate the rate of reaction by means of the Polanyi-Wigner equation. Topley (*Proc. Roy. Soc.*, 1932, *A*, **136**, 413), who discovered this relationship independently, has applied it in various forms to the endothermic changes $Ag_2CO_3 \longrightarrow Ag_2O + CO_2$ and $CuSO_4,5H_2O \longrightarrow CuSO_4,H_2O + 4H_2O$, and obtains as good an agreement between the calculated and experimental rates as could be expected in view of uncertainties in the area of the interface. For lead and potassium azides, from the equation $dN/dt = N\nu e^{-E/RT}$, where $N = 6 \times 10^{14}$ N_3 ions/cm.^{2}, and ν = the frequency of vibration of the N_3 ion found experimentally, *viz.*, 2×10^{13}, the following values of the calculated and the experimental rates are obtained :

		Rate, mols./cm.^{2}/sec.	
	Temp.	Calc.	Exptl.
Lead azide	270°	$1·2 \times 10^{13}$	$5·3 \times 10^{15}$
Potassium azide	251	$2·0 \times 10^{13}$	$1·7 \times 10^{15}$

The discrepancies between the experimental and calculated values are no greater than those found by Topley for $CuSO_4,5H_2O$. They can be explained by assuming that the interface between the salt and its product is diffuse, for which assumption there is ample evidence in the case of potassium azide at higher temperatures. Although no very great accuracy can be ascribed to the above calculations, they are of interest in showing that there are no marked differences between the behaviour of lead and potassium azides, such as might have been expected from the sensitivity of the former and inertness of the latter.

Much higher rates of reaction per cm.^{2} of interface can be observed for potassium and sodium than for lead azide. The latter detonates in a vacuum at 290°, consequent upon the attainment of a rate of reaction much smaller than can be observed for the alkali azides without detonation occurring. This inertness of the alkali azides is probably related to the volatilisation of the metal atoms, which process will absorb energy. In the case of lead

azide, the production of a stable interface will prevent the evaporation of the metal, even momentarily, and hence there will be available in this case a greater fraction of the total energy of the reaction for the activation of adjacent molecules.

SUMMARY.

The thermal decomposition of potassium and sodium azides has been studied in a vacuum and in the presence of the alkali-metal vapour. The decomposition of the former in potassium vapour is very much more rapid than in a vacuum, but the catalytic effect of sodium vapour on the decomposition of the sodium salt is small. From the appearance of the partially decomposed solids, it is concluded that the reaction penetrates into the interior of the crystals at the higher temperatures. This process obeys the equation for chain reactions.

The activation energies of the processes occurring in metallic vapour have been measured, and the values compared with those for other azides. The bearing of these values on the sensitivity of the azides is discussed.

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THE UNIVERSITY, BRISTOL. [*Received, March 19th, 1936.*]

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151 *The Hydrogenation of Δ^9-Octadecenyl Δ^9-Octadecenoate (Oleyl Oleate).*

By T. P. HILDITCH and H. PAUL.

IT has been known for many years that, when an ester of a long-chain polyethenoid acid is hydrogenated in presence of nickel, palladium, etc., catalysts, hydrogen is usually added selectively to one or other of the double bonds present. The investigations of Lebedev *et al.* (J., 1925, **127**, 417; 1928, 823, 2190; 1929, 220; 1930, 321) showed that preferential hydrogenation also frequently results as a consequence of the extent to which different ethenoid carbon atoms are united with, for example, alkyl groups. More recently, further instances of selectivity have appeared in the hydrogenation of the mixed triglycerides of various natural fats. For example, the mixed palmito-oleo-(or linoleo-)-glycerides of olive or cotton-seed oil (Hilditch and Jones, J., 1932, 805) or of pig depot fat (Hilditch and Stainsby, *Biochem. J.*, 1935, **29**, 90) become converted into palmitostearins before tristearin (from oleolinoleins, stearodioleins, etc.) is produced in any quantity; and the progressive hydrogenation of rape oil triglycerides (mixed glycerides containing oleic, linoleic and erucic radicals) takes a somewhat different course from that of the corresponding mixture of methyl esters (*J. Soc. Chem. Ind.*, 1935, **54**, 331T). We considered, therefore, that it would be interesting to examine the progressive hydrogenation of the ester of a monoethenoid higher fatty acid with the corresponding monoethenoid alcohol and chose for this purpose octadecenyl oleate, prepared by the esterification of purified oleic acid (from olive oil) with purified oleyl (Δ^9-octadecenyl) alcohol (from sperm oil).

The ester was hydrogenated in presence of nickel on kieselguhr at 180° to four intermediate stages short of complete saturation, and the composition of the partly hydrogenated products was determined by oxidising them with potassium permanganate in acetone. Of the possible products of hydrogenation—*n*-octadecyl stearate, *n*-octadecyl oleate, *n*-octadecenyl stearate, and unchanged *n*-octadecenyl oleate—the first-named was isolated unchanged, after the oxidations, in a pure condition. The remainder were completely converted into acidic products, from which, after complete hydrolysis, it was at first hoped to recover quantitatively the *n*-octadecyl alcohol and stearic acid which were present. From the amounts of these three compounds the composition of each partly

hydrogenated ester could be determined. Actually, however, it was not found possible to obtain the stearic acid satisfactorily freed from traces of scission products (*n*-nonoic acid, 9-hydroxy-*n*-nonoic acid or azelaic acid), and only the proportions of *n*-octadecyl stearate, and of *n*-octadecyl alcohol which must have been present as oleate (or *iso*oleate), were found capable of accurate determination. From these, however, the mean unsaturation (iodine value) of the partly hydrogenated ester being known, the proportions of the remaining components—*n*-octadecenyl stearate and unaltered *n*-octadecenyl oleate—were readily calculated.

The results obtained are in Table I, in which the extent of hydrogenation is expressed as a percentage of total saturation and determined from the iodine values of the hydrogenated esters (the *n*-octadecenyl oleate used had an iodine value of 94·7).

TABLE I.

Composition of Partly Hydrogenated n-*Octadecenyl Oleate.*

Hydrogenated ester. I.V.	% Hydrogenation.	*n*-Octadecyl stearate, %.	*n*-Octadecyl oleate, %.	*n*-Octadecenyl stearate, %.	*n*-Octadeceny oleate, %.
64·6	32	12	22	18	48
52·3	45	24	22	20	34
37·4	61	40	19	22	19
20·0	79	65	13	14	8

These figures show that the course of the hydrogenation is largely non-selective; in this particular instance, however, the alcoholic ethenoid group is slightly more readily hydrogenated than the acidic ethenoid group. Formation of the fully saturated ester sets in from the commencement, and the relative proportions of saturated and mono-ethenoid esters present at each stage are not far from those which would be expected on the hypothesis that only one double bond was hydrogenated at each effective contact with the catalyst. The amounts of saturated ester (and therefrom of the half-saturated compounds and of unchanged ester) calculated on this basis for the four stages of hydrogenation given in Table I are compared with the observed figures in Table II.

TABLE II.

% Hydrogenation.	*n*-Octadecyl stearate.		*n*-Octadecyl oleate + *n*-octadecenyl stearate.		*n*-Octadecenyl oleate.	
	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.
32	10	12	44	40	46	48
45	20	24	50	42	30	34
61	37	40	48	41	15	19
79	62	65	34	27	4	8

The data in Table II (which are illustrated graphically in Figs. 1 and 2) show that the observed course of the hydrogenation approximates to that calculated from simple considerations of probability except in the following respects:

(a) The amount of fully saturated ester is slightly but consistently greater than would be expected; this is not surprising, since (notwithstanding vigorous agitation in the hydrogenation apparatus) it may be supposed that the chances of encounter between an ester molecule and a catalyst particle are somewhat greater in the case of a half-hydrogenated molecule leaving the catalyst surface, than in that of a di-unsaturated molecule which within the same period has escaped adsorption at the surface of a catalyst particle.

(b) Of the two monoethenoid groups present in the original ester, that in the alcoholic radical is slightly more readily attacked than that in the acid group. Compared with other recorded instances of hydrogenation of diethenoid derivatives, however, it may be said that there is relatively little selectivity in the hydrogenation of the Δ⁹-octadecenyl and Δ⁹-octadecenoic groups in the ester which we have studied.

EXPERIMENTAL.

The oleic acid employed was prepared from the mixed acids of olive oil, from which most of the saturated acids were first removed by crystallisation of the lead salts from alcohol. The

unsaturated acids recovered from the soluble lead salts were converted into lithium salts, which, after two crystallisations from 80% alcohol (Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 322T), were almost free from linoleate. The acid recovered from the purified lithium oleate was converted into the methyl ester and fractionally distilled in a vacuum to remove the small proportion of palmitic acid which had escaped the lead salt-alcohol separation. The main fraction of the methyl oleate yielded on hydrolysis almost pure oleic acid.

The octadecenyl alcohol was prepared from alcohols obtained by the hydrolysis of sperm blubber oil. The alcohol, still contaminated with cetyl alcohol after fractional distillation in a vacuum, was kept at 0° for some time and the deposited solids were removed by filtration at 0°. It then had an iodine value of 90·7 (theo., 94·8).

The purified acid (247 g.) and alcohol (203 g.) were heated under 15 mm. pressure at 180° in presence of camphor-β-sulphonic acid (0·5 g.) for an hour after perceptible evolution of water vapour had ceased. The resulting ester (396 g.), from which unchanged acid had been removed, had saponification equivalent 534·0 and iodine value 94·7 (Calc. for $C_{36}H_{68}O_2$: saponification equiv., 532; iodine value, 95·5).

FIG. 1.

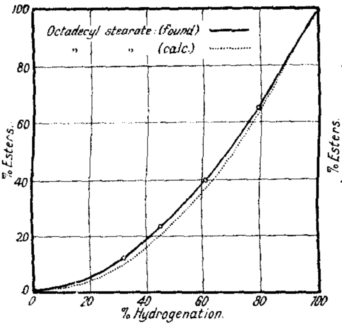
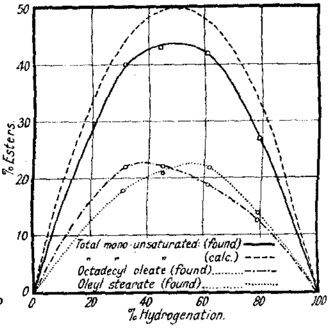


FIG. 2.



The ester was hydrogenated, in quantities of 80 g., a nickel–kieselguhr catalyst being used at 180° in an agitation apparatus connected with hydrogen inlet and exit meters in order to obtain products of the desired iodine values (cf. Table I).

The proportions of octadecyl stearate and of octadecyl oleate in the partly hydrogenated esters were determined by the following procedure. The ester (50 g.) was dissolved in acetone (500 g.) and oxidised under reflux by the addition of powdered potassium permanganate until the iodine value of the recovered neutral (unoxidised) product was below 1. After removal of all acidic products of oxidation there was thus obtained the octadecyl stearate which had been formed during hydrogenation. The whole of the alkaline (carbonate) aqueous extracts and washings obtained in this process were carefully hydrolysed with excess of caustic potash and then extracted with ether in order to recover any octadecyl alcohol thus liberated. This portion of the saturated alcohol must have been present as oleate and from its weight the corresponding weight of its oleic ester follows.

Similarly, after the extracted aqueous liquor from the preceding had been acidified, it was originally hoped to determine the stearic acid present; but, as already mentioned, a good quantitative separation of this acid from the mixture of azelaic, nonoic and hydroxynonoic acids also present was not satisfactorily achieved. Sufficient data were already available, however, to determine the proportions of the remaining components. The iodine value of the mixture of these was calculated from that of the original hydrogenated ester and its observed contents of saturated ester and of octadecyl oleate (iodine value 47·6), and from this iodine value the amounts of octadecenyl stearate (iodine value 47·6) and of octadecenyl oleate (iodine value 94·7) were, in turn, calculated. The octadecyl stearate obtained from the four products

melted, after crystallisation from acetone, at 58·5—59°; the octadecyl alcohol recovered from the acidic products of oxidation melted in each case (after crystallisation from alcohol) at 58°. Some details of these analyses are in Table III.

TABLE III.

Composition of Partly Hydrogenated Esters.

Iodine value of esters	64·6	52·3	37·4	20·0
Wt. oxidised (g.)	50·58	24·68	51·11	51·21
Octadecyl stearate isolated (g.)	6·05	5·87	20·51	33·59
,, alcohol ,, (g.)	5·50	2·72	4·79	3·35
whence octadecyl oleate (g.)	10·87	5·38	9·47	6·62
Octadecenyl stearate + ,, oleate } Iodine value (calc.)	81·7	77·0	69·2	64·4

	g.	%.	g.	%.	g.	%.	g.	%.
Octadecyl stearate	6·05	12	5·87	24	20·51	40	33·59	65
,, oleate	10·87	22	5·38	22	9·47	19	6·62	13
Octadecenyl stearate	9·29	18	5·05	20	11·44	22	7·08	14
,, oleate	24·37	48	8·38	34	9·69	19	3·92	8

We thank the Department of Scientific and Industrial Research for a grant to one of us (H. P.) during the course of the work.

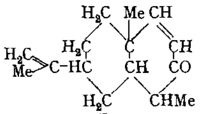
UNIVERSITY OF LIVERPOOL. [*Received, March 19th*, 1936.]

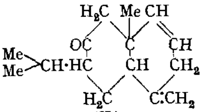
152. α-*Cyperone, a Sesquiterpene Ketone from the Oil of* Cyperus rotundus.

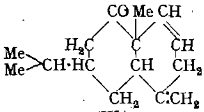
By A. E. BRADFIELD, B. H. HEGDE, B. SANJIVA RAO, J. L. SIMONSEN, and (in part) A. E. GILLAM.

ALTHOUGH the oil from the tubers of *Cyperus rotundus* has been frequently investigated, it is only recently (Hegde and Rao, *J. Soc. Chem. Ind.*, 1935, **54**, 387T) that the higher-boiling fractions have been shown to consist largely of sesquiterpene ketones. The main constituent, *α-cyperone*, can be purified readily through its *semicarbazone*, m. p. 216°, and has the composition $C_{15}H_{22}O$. It is dicyclic and contains two ethylenic linkages, yielding on catalytic hydrogenation *tetrahydro-α-cyperone*. Like eremophilone (J., 1932, 2744), it is a derivative of eudalene, since *dihydro-α-cyperol* yields this hydrocarbon on dehydrogenation with selenium.

It will now be shown that α-cyperone must be represented by (I), although its somewhat anomalous reactions led us originally to the erroneous conclusion that it had probably either formula (II) or (III) (compare J., 1935, 785).


(I.)


(II.)

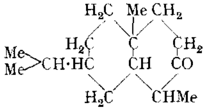

(III.)

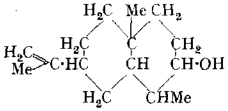
It was readily proved that one of the ethylenic linkages must be present as an exocyclic methylene group. Dihydro-α-cyperol, obtained by the reduction of α-cyperone with sodium and alcohol, whereby the keto-group and one ethylenic linkage were reduced simultaneously, on oxidation with ozone yielded formaldehyde and a ketonic alcohol, from which, by further oxidation with chromic acid, a colourless diketone, $C_{14}H_{22}O_2$, was prepared. Since neither the keto-alcohol nor the diketone gave bromoform with sodium hypobromite or iodoform with Fuson's reagent (Fuson and Tullock, *J. Amer. Chem. Soc.*, 1934, **56**, 1638), it appeared unlikely that the parent alcohol could contain an *iso*propenyl group, a deduction which

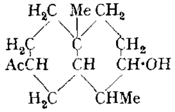
seemed to receive support from the absence of acetone from the oxidation products. It was assumed, therefore, that the methylene group was attached directly to the ring as in (II) or (III), but this assumption became doubtful when it was found that *dihydro-α-cyperyl* 3 : 5-*dinitrobenzoate* gave on ozonolysis a *ketone*, $C_{21}H_{26}O_7N_2$, m. p. 148—149°, from which iodoform was obtained on oxidation with Fuson's reagent.

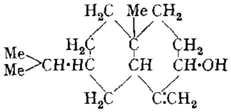
In view of these contradictory results it became necessary to establish directly the position of the carbonyl group. This was effected by treating tetrahydro-α-cyperone with methylmagnesium iodide and dehydrogenating the alcohol so obtained with selenium, whereby 1 : 2-dimethyl-7-*iso*propylnaphthalene was formed. The identity of this hydrocarbon was proved by a comparison of the *picrate*, m. p. 92—93°, and the s.-*trinitrobenzene* derivative, m. p. 108—110°, with synthetic specimens.

Since tetrahydro-α-cyperone was thus rigidly proved to be 1 : 10-dimethyl-7-*iso*propyl-decal-2-one (IV), it followed that dihydro-α-cyperol must be the related *iso*propenyl derivative (V), this structure alone explaining the formation of the ketone (VI) which would yield iodoform on oxidation with Fuson's reagent. The only alternative formula containing a methylene group (VII) is impossible, since an ethylenic linkage in this position would have been in the αβ-position to the original carbonyl group and would, therefore, have been reduced by sodium and alcohol.

(IV.) 

 (V.)

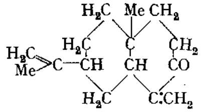
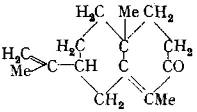
(VI.) 

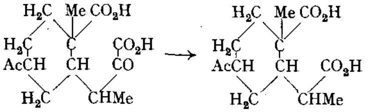
 (VII.)

It is now only necessary to ascertain the position of the second ethylenic linkage. Here again it was found that the evidence was conflicting. The reduction of this linkage with sodium and alcohol implies either that the two ethylenic linkages are conjugated with each other or that the carbonyl group has an ethylenic linkage in the αβ-position. On the one hand, the conjugation of the two ethylenic linkages is rendered highly improbable by the fact that the hydrocarbon *α-cyperene*, obtained from α-cyperone semicarbazone by the Wolff–Kishner reaction, could not be reduced by sodium in either ethyl or amyl alcohol solution. On the other hand, no direct evidence of conjugation with the carbonyl group was forthcoming. The ketone does not yield a derivative with hydrogen sulphide in the presence of alcoholic ammonia, or react with hydrogen cyanide (Lapworth and Clarke, J., 1906, **89**, 1872), and with hydrogen peroxide in alkaline solution no oxide is formed. In the last reaction, the greater part of the ketone was recovered as β-*cyperone* (see p. 674); a small quantity of a crystalline *keto-acid*, $C_{13}H_{20}O_3$, m. p. 112°, was, however, formed, the constitution of which is discussed on p. 669. Nevertheless, we conclude that conjugation with the carbonyl group is the more likely alternative, since negative results with the tests for an αβ-ethylenic linkage enumerated above are of doubtful diagnostic value. This conclusion is supported by a study of the absorption spectrum of α-cyperone (p. 676), and by the apparently abnormal formation of a hydroxymethylene derivative, discussed below, and it is in harmony with the course of the oxidation of the ketone and its derivatives.

This conclusion being accepted, α-cyperone must be represented by either (I), (VIII), or (IX). A study of the ozonolysis products of α-cyperone and of its semicarbazone showed (I) to be correct. The former yields, in addition to formaldehyde, a liquid dibasic keto-acid, $C_{13}H_{20}O_5$, the *dimethyl* ester of which was characterised by its *semicarbazone*, m. p. 245—246°. This acid must have the structure (XI), having been formed from the primary

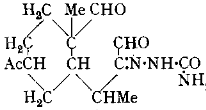
product of the oxidation (X) which, being an α-keto-acid, would be readily oxidised by the hydrogen peroxide generated during the decomposition of the ozonide. The formation of this acid excludes formulæ (VIII) and (IX).

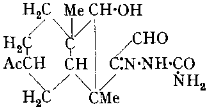
(VIII.)   (IX.)

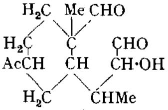
(X.)  (XI.)

Ozonolysis of α-cyperone semicarbazone gave a *semicarbazone*, $C_{15}H_{23}O_4N_3$, m. p. 185—187°. To this substance, which is a powerful reducing agent, we assign either formula (XII) or (XIII), its formation providing further proof that only one of the ethylenic linkages in α-cyperone is exocyclic.

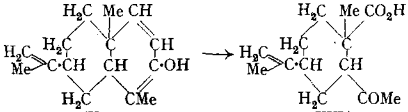
During the ozonolysis of an impure specimen of dihydro-α-cyperol, which evidently contained some α-cyperol, the related alcohol (XIV) was formed; it was isolated as a *di-* or *tri-phenylsemicarbazone*, m. p. 222—223°.

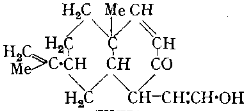

(XII.)


(XIII.)


(XIV.)

It was mentioned above that by the oxidation of α-cyperone with hydrogen peroxide in alkaline solution a keto-acid, $C_{13}H_{20}O_3$, was obtained. There can be little doubt that this acid is 6-*acetyl*-1-*methyl*-4-iso*propenyl*cyclo*hexane*-1-*carboxylic acid* (XVI), having been formed by the oxidation of the enolic form (XV) of the ketone.


(XV.) (XVI.)


(XVII.)

Although the reactions outlined above are in full accord with the structure (I) assigned to α-cyperone, a serious difficulty arises from the fact that the ketone gives an excellent yield of a liquid hydroxymethylene derivative, 2 : 4-*dinitrophenylhydrazone*, m. p. 159—160°, a reaction usually regarded as providing a sure indication of the presence of the group $-CH_2 \cdot CO-$. This group is not present in formula (I). By catalytic hydrogenation of the hydroxymethylene derivative, which was slow and incomplete, followed by reduction with sodium and alcohol, a substance was obtained which, on dehydrogenation with selenium, gave a hydrocarbon, $C_{15}H_{18}$, as shown by the analysis of the *picrate*, m. p. 102·5—104°, and the s.-*trinitrobenzene* derivative, m. p. 116—118°. If these reactions have proceeded normally, the hydrocarbon should be a naphthalene derivative with a methyl group in place of the hydroxymethylene group. The derivatives obtained were, however, not identical with the corresponding derivatives of 1 : 3-dimethyl-7-*iso*propylnaphthalene (see below), a fact which supports the conclusion that the carbon atom 3 (I) does not carry two

hydrogen atoms. The picrate of the hydrocarbon $C_{15}H_{18}$ has the same melting point as the picrate of 1 : 4-dimethyl-7-*iso*propylnaphthalene (Ruzicka, Pieth, Reichstein, and Ehmann, *Helv. Chim. Acta*, 1933, **16**, 268). By the kindness of Professor L. Ruzicka we have been able to make a direct comparison and we find that the two picrates are not identical, a mixed melting point determination showing a depression of 15—20°. Moreover, the melting points of the *s*.-trinitrobenzene derivatives differ widely.

It appeared to us possible that the hydroxymethylene group might have been introduced on the methyl group attached to the carbon atom in the α-position to the carbonyl group. If this assumption were correct, the substance would be represented by (XVII) and should on reduction, followed by dehydrogenation, yield 1-ethyl-7-*iso*propylnaphthalene. Synthesis of this substance and a comparison of its crystalline derivatives with the derivatives of the hydrocarbon $C_{15}H_{18}$ obtained from hydroxymethylenecyperone showed this assumption to be incorrect. We are at present unable to assign a structure to this naphthalene hydrocarbon or to account for the formation of the hydroxymethylene derivative. If the hydrocarbon is a dimethyl*iso*propylnaphthalene, it can only be 1 : 8-dimethyl-7-*iso*propylnaphthalene, since the other isomeric hydrocarbons are known (see below). It is intended to synthesise this hydrocarbon. We know of no analogy for the formation of a hydroxymethylene derivative from a ketone in the absence of an adjacent $-CH_2$ group, although we may instance the abnormal behaviour of the αβ-unsaturated ketones, piperitone (Earl and Read, J., 1926, 2072) and ψ-codeionone (Lutz and Small, *J. Amer. Chem. Soc.*, 1935, **57**, 2652) with benzaldehyde.

Although α-cyperone can be readily purified by distillation, it is isomerised by prolonged digestion with oxalic or phthalic acid or by the action of alkali to yield an isomeric ketone, *β-cyperone*, from which a number of derivatives have been prepared. This ketone can only differ stereochemically from α-cyperone, since its *semicarbazone* yields on oxidation with ozone the same substance as α-cyperone semicarbazone. We would suggest that they differ in the spatial arrangement of the methyl group adjacent to the carbonyl group and that they are therefore related as menthone and *iso*menthone.

Prior to the experiments recorded in this paper Ruzicka and his collaborators (*loc. cit.*) synthesised 1 : 4- and 1 : 5-dimethyl-7-*iso*propylnaphthalene. We have now synthesised the 1 : 2- and the 1 : 6-isomeride and have prepared 1 : 3-dimethyl-7-*iso*propylnaphthalene by the dehydrogenation of the product obtained by the action of methylmagnesium iodide on tetrahydroeremophilone. For the synthesis of 1 : 2-dimethyl-7-*iso*propylnaphthalene, 2-methyl-7-*iso*propyl-1 : 2 : 3 : 4-tetral-1-one was prepared by the condensation of *homocuminyl bromide* with ethyl potassiomethylmalonate, followed by ring closure with sulphuric acid. Treatment of the resulting ketone with methylmagnesium iodide, followed by dehydrogenation with selenium, gave the required hydrocarbon. As the starting point for the synthesis of the 1 : 6-isomeride, *o*-tolylacetyl chloride was condensed with *iso*propylzinc iodide to give *o-methylbenzyl* iso*propyl ketone*, which was converted, by condensation with ethyl α-bromopropionate and replacement of the hydroxyl group by hydrogen by the usual series of reactions, into *ethyl γ-o-tolyl-α-methyl-β-*iso*propylbutyrate*. Ring closure of the ester with sulphuric acid gave 2 : 5-dimethyl-3-*iso*propyl-1 : 2 : 3 : 4-tetral-1-one, which, after reduction with sodium and alcohol, was dehydrogenated with selenium to the hydrocarbon.

In the following table we list the characteristic derivatives of these isomeric naphthalene hydrocarbons.

Hydrocarbon.	Picrate, m. p.	Styphnate, m. p.	*s*.-Trinitrobenzene, m. p.
1 : 2-Dimethyl-7-*iso*propyl	92—93·5°	—	108—110°
1 : 3- „	113—114·5	—	141—142
1 : 4- „	102·5—103	—	144·5—145·5 *
1 : 5- „	115·5—116·5	—	145—147 *
1 : 6- „	124—126	141—142°	—
1-Ethyl-7-*iso*propyl	65—67		79—81

* Ruzicka, Pieth, Reichstein, and Ehmann, *loc. cit.*

The derivatives of the synthetic 1 : 5-dimethyl-7-*iso*propylnaphthalene and the 1 : 3-dimethyl-7-*iso*propylnaphthalene from tetrahydroeremophilone have almost identical

melting points. We have been able by the kindness of Professor Ruzicka to make a direct comparison of these derivatives. We find that, though there is no actual depression, the mixed melting points are decidedly less sharp than those of the pure individuals.

For the reasons already given (p. 670), we have synthesised also 1-ethyl-7-*iso*propyl-naphthalene. This was prepared from 7-*iso*propyl-1 : 2 : 3 : 4-tetral-1-one (obtained by the condensation of homocuminyl bromide with ethyl potassiomalonate, followed by ring closure) by the action of ethylmagnesium iodide, followed by dehydrogenation with selenium.

EXPERIMENTAL.

The crude essential oil * (ketone content, 33—54%) was treated with semicarbazide acetate, a solid semicarbazone, corresponding to approximately 54% of the total ketone content, separating; this, crystallised from alcohol, gave pure *α-cyperone semicarbazone* (see below). After separation of the solid semicarbazone the non-ketonic constituents of the oil were removed by steam; a liquid semicarbazone remained which could not be purified. This semicarbazone was only partly hydrolysed by oxalic or phthalic acid; it gave, in addition to a further quantity of α-cyperone, a ketone, b. p. 145—146°/5 mm., $d_{30°}^{30°}$ 0·9879, $n_D^{30°}$ 1·5138, $[\alpha]_D^{30°}$ + 28·5°, $[R_L]_D$ 66·3 (Found: C, 82·2; H, 9·8. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%). No crystalline derivatives could be prepared from this ketone, so its homogeneity is doubtful.

α-Cyperone.—The ketone, prepared from the pure semicarbazone by hydrolysis with oxalic acid in acetone solution and purified by distillation in steam, was a colourless mobile oil, b. p. 177°/20 mm., $d_{25°}^{25°}$ 0·9946, $n_D^{25°}$ 1·5283, $[\alpha]_{5461}$ + 138°, $[\alpha]_{5780}$ + 118·6°, $[R_L]_D$ 67·53 (calc., 66·15) (Found: C, 82·0; H, 10·3. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%). Oxidation with percamphoric acid proceeded very slowly; after 24 hours, 1·2 atoms of oxygen per molecule had been absorbed and after 8 days about 1·7. The *semicarbazone*, prepared from the recovered ketone, crystallised from methyl alcohol in serrated prisms, m. p. 216°; $[\alpha]_{5461}$ + 178° in chloroform (*c*, 5·0) (Found: C, 69·9; H, 9·4; N, 15·4. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·1; N, 15·3%). The *oxime* separated from methyl alcohol in long prismatic needles, m. p. 150·5°; $[\alpha]_{5461}$ + 134° in ethyl alcohol (*c*, 1·35) (Found: C, 77·2; H, 10·0; N, 6·2. $C_{15}H_{23}ON$ requires C, 77·3; H, 9·9; N, 6·0%). The 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol–ethyl acetate in soft red needles with a bronze reflex, m. p. 209—210° (Found: C, 63·6; H, 6·6. $C_{21}H_{26}O_4N_4$ requires C, 63·6; H, 6·6%). The *nitroguanylhydrazone* was deposited from alcohol in clusters of long needles, decomp. 203—204°; $[\alpha]_D$ + 196° in chloroform (*c*, 2·5) (Found: N, 21·7. $C_{16}H_{25}O_2N_5$ requires N, 21·9%).

Hydroxymethylene-α-cyperone.—To a well-cooled solution of α-cyperone (3 g.) in ether (50 c.c.) containing finely divided sodium (0·35 g.) in suspension, amyl formate (1·8 g.) was added. After 12 hours, the greater part of the sodium having dissolved, ice was added, and the brown alkaline solution separated. After extraction with ether, the solution was acidified with acetic acid and the oil which separated was dissolved in ether. Evaporation of the dried ethereal extract left hydroxymethylene-α-cyperone as a viscid brown oil giving an intense reddish-violet colour with alcoholic ferric chloride. The 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol–ethyl acetate in rosettes of thin, dark brown prisms, m. p. 159—160° (Found: C, 62·1; H, 5·9. $C_{22}H_{26}O_5N_4$ requires C, 62·0; H, 6·1%).

Reduction of α-Cyperone.—(i) *Catalytic*. The ketone (5·2 g.) in ethyl alcohol (50 c.c.) was shaken with hydrogen in the presence of palladium-norit (Pd, 10%), 1041 c.c. (1·95 mols.) of hydrogen being absorbed. The *tetrahydro-α-cyperone* had b. p. 151—152°/14 mm., $d_{25°}^{25°}$ 0·9597, $n_D^{25°}$ 1·4871, $[\alpha]_{5461}$ + 14·8° (mic.),† $[\alpha]_{5780}$ + 12·4° (mic.), $[R_L]_D$ 66·42 (calc., 67·08) (Found: C, 81·2; H, 11·6. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%). The *semicarbazone* separated from methyl alcohol as a crystalline powder, decomp. 173—175° (Found: C, 69·3; H, 10·5. $C_{16}H_{29}ON_3$ requires C, 68·8; H, 10·4%). The *oxime* was deposited from alcohol in soft needles, m. p. 116—117·5° (Found: C, 75·4; H, 11·5. $C_{15}H_{27}ON$ requires C, 75·9; H, 11·4%). The 2 : 4-*dinitrophenylhydrazone* formed clusters of fine orange needles, m. p. 151—152° (Found: C, 62·7; H, 7·6. $C_{21}H_{30}O_4N_4$ requires C, 62·7; H, 7·5%). Hydroxymethylene tetrahydro-α-cyperone, prepared in the usual manner, was a mobile oil giving with alcoholic ferric chloride an

* The percentage of α-cyperone present in the oil was highest in the oils having a high dextrorotatory power. Some specimens of the oil were lævorotatory and gave no α-cyperone semicarbazone although they contained as much as 35% of ketones. This point is being further investigated.

† Rotations were observed in a 1 dm. tube, except those followed by "(mic.)," for which a ½ dm. micro-tube was used.

intense purple-red colour. The 2 : 4-*dinitrophenylhydrazone* separated from alcohol–ethyl acetate in red needles with a coppery sheen, m. p. 182—183° (Found : C, 61·7; H, 6·8 $C_{21}H_{30}O_5N_4$ *requires C,* 61·4; *H,* 7·0%).

(ii) *With sodium and alcohol.* To a solution of α-cyperone (10 g.) in ethyl alcohol (400 c.c.) sodium (40 g.) was added as rapidly as possible, the reaction being completed by heating on the water-bath. After removal of the ethyl alcohol in steam, the sesquiterpene alcohol was extracted with ether, the ether dried and evaporated, and the residual oil distilled under diminished pressure; *dihydro-α-cyperol* was obtained as an extremely viscid oil, b. p. 167—168°/15 mm., $n_D^{25°}$ 1·5121, $[\alpha]_{5461}$ + 17·7° (in ethyl alcohol; *c*, 2·26) (Found : C, 80·7; H, 11·4 $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%). The 3 : 5-*dinitrobenzoate*, prepared by treating the alcohol with 3 : 5-dinitrobenzoyl chloride in pyridine solution, crystallised from alcohol in soft silky needles, m. p. 157—158° (Found : C, 63·5; H, 6·6. $C_{22}H_{28}O_6N_2$ requires C, 63·5 H, 6·7%).

Dehydrogenation of Dihydro-α-cyperol.—The alcohol (7·5 g.) was heated with selenium first at 200° and later at 250° for 40 hours. From the product, eudalene was isolated and identified as the picrate, m. p. 91—92°, both alone and in admixture with an authentic specimen; the styphnate had m. p. 117—118°.

Oxidation of α-Cyperone.—(i) *With ozone.* The ketone (11 g.) in ethyl acetate (55 c.c.) cooled in ice, was ozonised, the issuing gases being led through water, which at the end of the experiment gave the dimedone test for formaldehyde. After evaporation of the solvent, the ozonide was decomposed with water and gave a keto-acid (7·3 g.). This was esterified with diazomethane; the liquid *ester*, b. p. 190—197°/11 mm., was not quite pure (Found : C, 64·3 H, 8·4. $C_{15}H_{24}O_5$ requires C, 63·4; H, 8·5%). The *semicarbazone*, which crystallised from alcohol, decomposed at 245—246° (Found : C, 56·8; H, 7·9. $C_{16}H_{27}O_5N_3$ requires C, 56·4 H, 7·9%).

The acid obtained by the hydrolysis of the ester was a yellow oil, which reduced Fehling's solution but gave no crystalline derivatives with carbonyl reagents. With sodium hypobromite its alkaline solution gave only a faint turbidity.

(ii) *With hydrogen peroxide.* To the ketone (2·4 g.) in methyl alcohol (25 c.c.), a mixture of 4*N*-sodium hydroxide (2·8 c.c.) and 15% hydrogen peroxide (5·5 c.c.) was added; considerable heat was generated. After 12 hours water was added, and the methyl alcohol removed in steam. The neutral oil (β-cyperone) was extracted with ether, and the alkaline solution acidified; a viscid oil separated. This was dissolved in ether, removal of the solvent yielding an oil which partly crystallised. The acid was dissolved in aqueous ammonia, the gummy calcium salt precipitated by calcium chloride removed, the filtrate acidified, and the liquid acid extracted with ether. The oil remaining after removal of the solvent solidified and after draining on porous porcelain was recrystallised from either formic acid or methyl alcohol. The *acid* separated in fine needles, m. p. 112°; $[\alpha]_{5461}$ + 62·6° in methyl alcohol (*c*, 2·22) (Found : C, 69·1; H, 8·7 $C_{13}H_{20}O_3$ requires C, 69·6; H, 8·9%). It decolorised potassium permanganate in alkaline solution, but was not attacked by sodium hypobromite or by Fuson's reagent. The *semicarbazone* crystallised from methyl alcohol in long prisms, decomp. 180—181° (Found : C, 59·9; H, 8·2. $C_{14}H_{23}O_3N_3$ requires C, 59·8; H, 8·2%). The *phenylsemicarbazone* separated from ethyl alcohol in well-formed prisms, decomp. 200° (Found : C, 67·1; H, 7·6. $C_{20}H_{27}O_3N_3$ requires C, 67·2; H, 7·6%).

Oxidation of α-Cyperone Semicarbazone with Ozone.—The semicarbazone (2 g.) was suspended in acetic acid (40 c.c.), and ozone passed through at room temperature until all the solid had dissolved. The solvent was removed under diminished pressure, and the residual oil stirred with a little methyl alcohol; the crystalline solid obtained, recrystallised from alcohol, separated in well-formed needles, decomp. 185—187° (Found : C, 58·2; H, 7·4. $C_{15}H_{23}O_4N_3$ requires C, 58·3; H, 7·4%). The *semicarbazone* gave no colour with ferric chloride; it reduced Fehling's solution and ammoniacal silver nitrate. Its alcoholic solution gave with semicarbazide acetate an amorphous powder which was very sparingly soluble in all the ordinary solvents and could not be recrystallised (Found : C, 41·9, 42·1; H, 6·8, 6·6; N, 31·0%).

Oxidation of Dihydro-α-cyperol with Ozone.—The alcohol (5·1 g.) in ethyl acetate (20 c.c.), cooled in ice, was oxidised with ozone. Formaldehyde was identified in the issuing gases by preparation of the dimedone derivative. After evaporation of the solvent, the ozonide was decomposed by boiling water and separated into acid and neutral portions. No crystalline derivatives of the acid fraction could be prepared and this was not further examined. The neutral oil (3·1 g.), b. p. 200—205°/17 mm., was oxidised to the corresponding diketone by chromic acid in acetic acid solution. This was a viscid oil, which gave no bromoform with sodium

hypobromite in alkaline solution and did not react with Fuson's reagent. The *dioxime* crystallised from butyl alcohol in small hexagonal plates, decomp. 258—259°, sintering at 247° (Found: C, 67·0; H, 9·7. $C_{14}H_{24}O_2N_2$ requires C, 66·7; H, 9·5%). The *disemicarbazone* separated from the same solvent as a microcrystalline powder, decomp. 251—252° (Found: C, 56·8; H, 8·3. $C_{16}H_{28}O_2N_6$ requires C, 57·1; H, 8·3%).

In a preliminary experiment in which an impure specimen of the alcohol, containing some α-cyperol, was used, the neutral ozonolysis product gave a *di- or tri-phenylsemicarbazone*, decomp. 222—223°, which crystallised from butyl alcohol (Found: C, 64·5, 64·7; H, 6·7, 6·5. $C_{28}H_{36}O_4N_6$ requires C, 64·6; H, 6·9. $C_{35}H_{43}O_4N_9$ requires C, 64·4; H, 6·6%). The constitution of this substance is referred to on p. 669.

Oxidation of Dihydro-α-cyperyl 3 : 5-*Dinitrobenzoate*.—Ozone was passed through a solution of the benzoate (2·5 g.) in ethyl acetate (25 c.c.) until it was present in excess. The issuing gases contained a considerable quantity of formaldehyde, identified as the dimedone derivative (0·2 g.). After removal of the ethyl acetate the ozonide was decomposed by boiling water, the small amount of acid present was neutralised with potassium bicarbonate, and the oil which had separated was extracted with ether. Evaporation of the dried extract gave a gum (2·2 g.), which, except for a small quantity of resinous impurity, crystallised from acetic acid (70%) in fine needles, decomp. 143° with previous sintering. After two further recrystallisations from the same solvent and two from alcohol, the *ketone* was obtained in soft needles, m. p. 148—149°, not depressed by dihydro-α-cyperyl 3 : 5-dinitrobenzoate (Found: C, 60·2; H, 6·1. $C_{21}H_{26}O_7N_2$ requires C, 60·3; H, 6·2%). The ketone reacted readily with the ordinary carbonyl reagents, but crystalline derivatives could not be prepared. With Fuson's reagent, iodoform, m. p. 119—120°, was formed; the alkaline solution on acidification deposited a gummy acid, from which a small quantity of 3 : 5-dinitrobenzoic acid was separated, but the main product of the oxidation could not be crystallised.

Conversion of Tetrahydro-α-cyperone into 1 : 2-*Dimethyl*-7-iso*propylnaphthalene*.—The ketone (9·7 g.) was treated with the Grignard reagent prepared from magnesium (1·15 g.) and methyl iodide (6·8 g.). As the product still contained a trace of ketone, it was treated with a further quantity of the reagent. The final product, a mixture of unsaturated hydrocarbon and alcohol, b. p. 137—150°/11 mm., was dehydrogenated by heating with selenium first at about 200° and finally at 300° for 40 hours. The product, b. p. 140—150°/12 mm., gave a *picrate* crystallising from alcohol in feathery orange-yellow needles, m. p. 92—93° (Found: C, 58·9; H, 4·8. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9%), and a s.-*trinitrobenzene* derivative separating from alcohol in yellow needles, m. p. 107—109° (Found: C, 60·9; H, 4·9. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%). These derivatives were identical in all respects with the corresponding derivatives of 1 : 2-dimethyl-7-*iso*propylnaphthalene the synthesis of which is described on p. 674.

Reduction and Dehydrogenation of Hydroxymethylene-α-cyperone.—Reduction of hydroxymethylene-α-cyperone (10 g.) by hydrogen in the presence of palladium-norit under 3 atm. pressure was very slow and after 70 hours only about half the calculated quantity of hydrogen had been absorbed. The reduction was therefore completed with sodium and alcohol, and the very viscid oil obtained (5 g.) dehydrogenated by heating with selenium at 300—320° for 23 hours. The product, b. p. 140—160°/10 mm., yielded a *picrate*, which crystallised from methyl alcohol in short orange needles, m. p. 102·5—104° (Found: C, 59·2; H, 5·3. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9%), and a s.-*trinitrobenzene* derivative crystallising from alcohol in bright yellow needles, m. p. 116—118° (Found: C, 61·4; H, 5·2. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%).

α-Cyperene.*—α-Cyperone semicarbazone (2 g.) was heated with sodium ethoxide (ethyl alcohol, 3 c.c.; sodium, 0·25 g.) at 200° for 6—7 hours. The product from several such experiments was isolated by steam distillation and purified by distillation over sodium, the *hydrocarbon*, b. p. 132—133°/15 mm., obtained being not quite pure (Found: C, 87·2; H, 11·5. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%). Oxidation with ozone in ethyl acetate solution at 0° gave formaldehyde (dimedone test), but no acetone was formed on decomposition of the ozonide with hot water. The main product of the oxidation was a neutral substance, which gave amorphous derivatives with the usual carbonyl reagents. It reduced ammoniacal silver nitrate solution and gave a positive iodoform test with Fuson's reagent, but no colour with ferric chloride. A small quantity of an acid was obtained also. This gave no crystalline derivatives with carbonyl group reagents, gave a positive Fuson test, but did not reduce ammoniacal silver nitrate solution and gave no colour with ferric chloride.

* The name cyperene has been given to a sesquiterpene of unknown constitution obtained by Kimura and Ohtani (*J. Pharm. Soc. Japan*, 1928, **48**, 128) from the rhizomes of *Cyperus rotundus*.

The hydrocarbon, b. p. 130—132°/14 mm., was recovered unchanged after treatment with sodium and ethyl or amyl alcohol and on titration with percamphoric acid it then showed an absorption of oxygen corresponding to 1·9 ethylenic linkages.

β-Cyperone.—As mentioned on p. 670, α-cyperone was isomerised when digested with an aqueous solution of oxalic acid for some hours, a change which was also effected by the action of methyl-alcoholic potassium hydroxide solution. The new ketone was converted into the *semicarbazone*, which crystallised from methyl alcohol in prisms, decomp. 207° (Found: C, 69·9; H, 9·0; N, 15·0. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·1; N, 15·3%). The semicarbazone was phototropic, becoming yellow on exposure to light, the colourless form being obtained after recrystallisation from methyl alcohol. β-*Cyperone*, regenerated from the semicarbazone by digestion with oxalic acid in acetone solution, was a colourless mobile oil, b. p. 175—176°/16 mm., $d_{25°}^{25°}$ 0·9945, $n_D^{20°}$ 1·5414, $[\alpha]_{5461}$ + 239° (Found: C, 82·2; H, 10·3. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%). The *oxime* crystallised from methyl alcohol in prismatic needles, m. p. 138°, $[\alpha]_{5461}$ + 217° in alcohol (*c*, 1·45) (Found: C, 76·9; H, 9·5; N, 5·8. $C_{15}H_{23}ON$ requires C, 77·3; H, 9·9; N, 6·0%). The 2 : 4-*dinitrophenylhydrazone* separated from alcohol–ethyl acetate in red needles with a metallic reflex, decomp. 218—219° (Found: C, 63·2; H, 6·5. $C_{21}H_{26}O_4N_4$ requires C, 63·6; H, 6·6%). The *nitroguanylhydrazone* crystallised from alcohol in needles, m. p. 197°; $[\alpha]_D$ + 220° in chloroform (*c*, 2·5) (Found: N, 21·6. $C_{16}H_{25}O_2N_5$ requires N, 21·9%). Ozonolysis of β-cyperone semicarbazone gave a semicarbazone, m. p. 185—187°, identical with that obtained by the ozonolysis of α-cyperone semicarbazone (compare p. 672) (Found: C, 58·0; H, 7·3%).

Synthesis of 1 : 2-*Dimethyl*-7-iso*propylnaphthalene.*—*Homocuminyl alcohol.* Homocumic acid was prepared quantitatively from the corresponding mandelic acid by reduction with tin and hydrochloric acid. The use of amalgamated zinc in place of tin gave inferior results.

Ethyl homocuminate (41·5 g.) in alcohol (300 c.c.) was added in one portion to sodium (29 g.). When the reaction had moderated, the mixture was maintained at 130° until all the sodium had dissolved. The ethyl alcohol was removed in a current of steam, and the cooled solution extracted with ether. After drying and removal of the solvent, *homocuminyl alcohol* (20·3 g.), b. p. 129°/10 mm., was obtained (Found: C, 80·4; H, 9·8. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). The p-*xenylcarbamate* crystallised from benzene–ligroin in fine needles, m. p. 144—145° (Found: C, 80·4; H, 7·0. $C_{24}H_{25}O_2N$ requires C, 80·2; H, 7·0%).

Homocuminyl bromide. Homocuminyl alcohol (34 g.) was added to phosphorus tribromide (28 g.), and the mixture heated on the water-bath for 2 hours. The product was decanted from the phosphorous acid into ice-water and recovered with ether. *Homocuminyl bromide* (42 g.), b. p. 136°/14 mm., was a pleasant-smelling mobile oil (Found: Br, 35·4. $C_{11}H_{15}Br$ requires Br, 35·3%).

Ethyl homocuminylmethylmalonate. To a suspension of ethyl methylpotassiomalonate (from ethyl methylmalonate, 24 g., and potassium, 5·3 g.) in benzene (50 c.c.), homocuminyl bromide (30 g.) was added, and the mixture heated on the water-bath for 100 hours. Isolated in the usual manner, *ethyl homocuminylmethylmalonate* (34 g.) was obtained as a somewhat viscid oil, b. p. 200°/13 mm. (Found: C, 71·0; H, 8·5. $C_{19}H_{28}O_4$ requires C, 71·2; H, 8·7%).

2-*Methyl*-7-iso*propyl*-1 : 2 : 3 : 4-*tetral*-1-*one.* The ester (38 g.) was heated on the water-bath with sulphuric acid (160 c.c.) and water (60 c.c.) for 3 hours. After dilution with water the ketone was extracted with ether, the solvent removed, and some unchanged ester hydrolysed by digestion with methyl-alcoholic potassium hydroxide solution. The ketone (10 g.), separated by the addition of water and extraction with ether, was a mobile colourless oil, b. p. 155—160°/12 mm. The *phenylsemicarbazone* crystallised from alcohol in prisms, m. p. 180—181° (Found: C, 75·4; H, 7·6. $C_{21}H_{25}ON_3$ requires C, 75·2; H, 7·5%). The 2 : 4-*dinitrophenylhydrazone* separated from alcohol–ethyl acetate in deep red prisms, frequently twinned, m. p. 177—178° (Found: N, 14·6. $C_{20}H_{22}O_4N_4$ requires N, 14·7%).

The above ketone (10 g.) was added to the Grignard reagent prepared from methyl iodide (15 g.) and magnesium (2·4 g.). After 24 hours, the solution was heated on the water-bath for 1 hour, and the product isolated in the usual manner. The oil (8 g.), b. p. 135—140/10 mm., consisted mainly of hydrocarbon and was dehydrogenated by heating with selenium (15 g.) at 300° for 28 hours, yielding 1 : 2-dimethyl-7-*iso*propylnaphthalene as a colourless oil, b. p. 149—151°/9 mm. The *picrate* crystallised from alcohol in orange-yellow needles, m. p. 92—93·5° (Found: N, 9·7. $C_{21}H_{21}O_7N_3$ requires N, 9·8%), and the *s.-trinitrobenzene* derivative from alcohol in yellow needles, m. p. 108—110° (Found: N, 9·8. $C_{21}H_{21}O_6N_3$ requires N, 10·2%).

1 : 3-*Dimethyl*-7-iso*propylnaphthalene.*—Tetrahydroeremophilone (11 g.) was added to the

Grignard reagent prepared from methyl iodide (17·7 g.) and magnesium (3 g.) and after 20 hours the solution was heated on the water-bath for 1 hour. The product (10·4 g.), isolated in the usual manner, had b. p. 145—150°/7 mm. It was dehydrogenated by heating with selenium at 300—310° for 24 hours. The hydrocarbon obtained gave a *picrate*, which crystallised from alcohol in silky orange-yellow needles, m. p. 113—114·5° (Found : C, 59·2; H, 4·8. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9%). The *s.-trinitrobenzene* derivative formed bright yellow needles, m. p. 141—142° (Found : C, 61·1; H, 5·0. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%).

Synthesis of 1 : 6-*Dimethyl*-7-iso*propylnaphthalene*.—o-*Methylbenzyl* iso*propyl ketone*. *o*-Tolylacetic acid was prepared from ω-bromo-*o*-xylene *via* the nitrile. A better return of the monobromo-compound on the *o*-xylene used was obtained by using less bromine than that given by Atkinson and Thorpe (J., 1907, 91, 1695). *o*-Xylene (75 g.) on treatment with bromine (90 g.) at 130° gave ω-bromide (77·3 g.), b. p. 110—114°/16 mm., and *o*-xylene (23 g.). *o*-Tolylacetyl chloride, prepared by the action of thionyl chloride on the acid, had b. p. 111—112°/16 mm.

A mixture of *iso*propyl iodide (60 g.), ethyl acetate (10 c.c.), and ligroin (b. p. 105—115°) (21 c.c.) was cautiously heated with a zinc–copper couple (50 g.) until the reaction began; the temperature was then gradually raised to 110° and maintained for 30 minutes. The solution of *iso*propylzinc iodide thus prepared was mixed with toluene (21 c.c.), decanted from the excess of the zinc–copper couple, and well cooled in ice in a vessel from which moisture was excluded. A mixture of *o*-tolylacetyl chloride (26·5 g.) and toluene (25 c.c.) was slowly added (mechanical stirring) and after addition was complete the solution was allowed to come slowly to room temperature, again cooled, and water added; the slight precipitate of zinc hydroxide was dissolved with dilute sulphuric acid. The product was extracted with ether, the extract washed three times with aqueous ammonia, then with water, dilute sulphuric acid and water, dried, and the ether removed. The residue was refluxed with alcoholic potassium hydroxide (KOH, 10 g.) to hydrolyse the ester formed as a by-product, and steam-distilled, and the oil which passed over was collected in ether. The hydrocarbon solvent was removed at 100 mm., and the residue distilled at 13 mm., o-*methylbenzyl* iso*propyl ketone*, b. p. 125—126°, $d_{25°}^{25°}$ 0·9652, $n_D^{25°}$ 1·5070, being obtained as a slightly greenish oil which became colourless on standing over-night (yield, 40%) (Found : C, 81·7; H, 9·1. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%). The *semicarbazone* crystallised from methyl alcohol in prisms, m. p. 128—129° (Found : C, 66·9; H, 8·3. $C_{13}H_{19}ON_3$ requires C, 66·9; H, 8·2%); the *phenylsemicarbazone* separated from alcohol in prismatic needles, m. p. 183° (Found : C, 73·7; H, 7·4. $C_{19}H_{23}ON_3$ requires C, 73·8; H, 7·4%).

Ethyl γ-o-*tolyl*-α-*methyl*-β-iso*propylbutyrate*. The ketone (28 g.) and ethyl α-bromopropionate (39 g.) were added to zinc (18·5 g.) covered with dry ether and the mixture was heated on the water-bath, the reaction being initiated by the addition of methylmagnesium iodide. After 6 hours the product was treated with ice and dilute hydrochloric acid, and the ether separated, washed with dilute sulphuric acid, potassium bicarbonate solution, dried, and evaporated. The residue, b. p. 165—195°/16 mm., was dehydrated by heating with potassium hydrogen sulphate (40 g.) for 2 hours at 195—200°. The product, without further purification, was reduced with hydrogen under 3 atms. in the presence of palladium-norit catalyst in alcoholic solution. After removal of the alcohol *ethyl* γ-o-*tolyl*-α-*methyl*-β-iso*propylbutyrate* distilled at 165°/13 mm. (Found : C, 78·0; H, 9·7. $C_{17}H_{26}O_2$ requires C, 77·9; H, 9·9%).

2 : 5-*Dimethyl*-3-iso*propyl*-1 : 2 : 3 : 4-*tetral*-1-*one*. The above-mentioned ester (24 g.) was heated on the water-bath with sulphuric acid (acid, 122·5 c.c.; water, 52·5 c.c.) for 1 hour, and the mixture poured into water. The oil was extracted with ether, the solvent removed, and the residue refluxed with an excess of alcoholic potassium hydroxide solution for 30 minutes. After addition of water, the ketone was again collected in ether, the solution dried, and the solvent removed; the ketone then had b. p. 185—190°/22 mm. The *phenylsemicarbazone* crystallised from alcohol in prismatic needles, m. p. 222—223° (Found : C, 75·2; H, 7·8. $C_{22}H_{27}ON_3$ requires C, 75·6; H, 7·7%).

The ketone (11 g.) in boiling ethyl alcohol (200 c.c.) was treated with sodium (20 g.); after reduction was complete, the ethyl alcohol was removed in steam, and the product extracted with ether. Without further purification the tetralol was dehydrogenated by heating with selenium at 280° for 15 hours. The 1 : 6-dimethyl-7-*iso*propylnaphthalene, after purification through the picrate, had b. p. 154—158°/13 mm. The *picrate* crystallised from ethyl alcohol in orange-red needles, m. p. 124—126° (Found : C, 59·6; H, 5·0. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9%). The *styphnate* was deposited from ethyl alcohol in silky orange-yellow needles, m. p. 141—142° (Found : C, 57·0; H, 4·8. $C_{21}H_{21}O_8N_3$ requires C, 56·9; H, 4·7%).

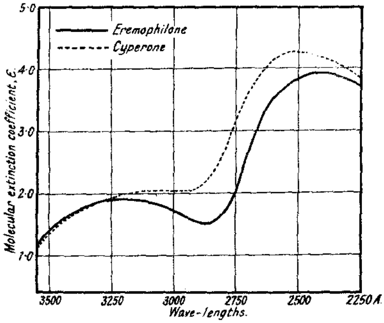
Synthesis of 1-*Ethyl*-7-*isopropylnaphthalene*.—*Ethyl homocuminylmalonate* was prepared from homocuminyl bromide under conditions similar to those used for the preparation of ethyl homo-

cuminylmethylmalonate (p. 674), ethyl methylmalonate being replaced by ethyl malonate. The ester (20 g. from the bromide, 20 g.) had b. p. 198°/13 mm. (Found: C, 70·4; H, 8·5. $C_{18}H_{26}O_4$ requires C, 70·6; H, 8·5%). *It was converted into 7-isopropyl-1 : 2 : 3 : 4-tetral-1-one, b. p. 158—160°/17 mm.*, with sulphuric acid under conditions similar to those described above. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in soft needles, m. p. 223—224° (Found: C, 62·1; H, 5·5. $C_{19}H_{20}O_4N_4$ requires C, 62·0; H, 5·4%).

The tetralone (6 g.) was treated with a Grignard reagent prepared from magnesium (2 g.) and ethyl iodide (12·5 g.), and the product, recovered in the usual manner, dehydrogenated by heating with selenium at 300—320° for 40 hours. From the crude 1-ethyl-7-*iso*propylnaphthalene, b. p. 135—145°/9 mm., a *picrate* was prepared in methyl-alcoholic solution, which crystallised from the same solvent, in which it was somewhat readily soluble, in deep yellow needles, m. p. 65—67°, although the melt did not become clear until the temperature was 20—30° higher. This m. p. was unchanged after several crystallisations, and further fractionation of the material in the mother-liquors failed to yield any indication of the presence of a second substance (Found: C, 59·0; H, 5·1. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9%). The *s.-trinitrobenzene* derivative crystallised from ethyl alcohol in yellow needles, m. p. 79—81° (Found: C, 61·7; H, 5·3. $C_{21}H_{21}O_6N_3$ requires C, 61·2; H, 5·1%).

The Absorption Spectrum of α-Cyperone and its Indications as to the Probable Structure of the Compound (By A. E. Gillam).

Before α-cyperone had been successfully reduced to a product of known constitution it was suggested that the nature of the absorption spectrum might throw some light on its molecular



structure. In particular it was important to know whether the C:O and the C:C linkages known to be present were conjugated or not.

The absorption spectrum was determined on a Hilger E_3 quartz spectrograph fitted with a Spekker photometer. The absorption curve (see fig.) will be seen to be made up of two bands: the one of low intensity and negligible persistence at 3000—3200 A. is due to a C:O group, and the short-wave band of high intensity is typical of a conjugated system of double bonds.

It was known that the compound was an unsaturated ketone, and if the C:O and C:C bonds were widely separated in the molecule one would expect only the absorption characteristic of the C:O group to be exhibited. Thus methylheptenone, $CHMe_2$:CH·CH_2·CH_2·CO·CH_3, has $\lambda_{max.}$ at 2780 A. and log $\varepsilon_{max.}$ = 1·72, data closely comparable with those of acetone ($\lambda_{max.}$ 2750 A., log $\varepsilon_{max.}$ = 1·23).

The results show that the absorption spectrum of α-cyperone is quite different from that of either acetone or methylheptenone, being in fact very similar to that of mesityl oxide (Morton, J., 1926, 719), a very simple αβ-unsaturated ketone. Various typical saturated and unsaturated ketones have also been examined by Menschik, Page, and Bossert (*Annalen*, **1933**, **495**, 225), who have demonstrated clearly that absorption of the type shown by mesityl oxide can be taken to indicate the presence of a C:O group conjugated with a C:C group. The evidence of absorption

spectra thus strongly supports the view that α-cyperone is an αβ-unsaturated ketone. In order to substantiate this further, the absorption spectrum of another compound closely analogous to α-cyperone, *viz.*, eremophilone, and definitely known to be an αβ-unsaturated ketone was examined and found to be closely similar to that of α-cyperone (see fig.). The following table shows some relevant numerical data for compounds with the chromophoric group C:C—C:O.

	" Ethylene " band.		" Ketone " band.		Literature.
	$\lambda_{max.}$, A.	Log ε.	$\lambda_{max.}$, A.	Log ε.	
Cholestenone	2430	4·30	3120	2·07	Heilbron, Morton, and Sexton, J., 1928, 719.
Mesityl oxide	2350	4·14	3130	1·74	Morton, *loc. cit.*
Eremophilone......	2430	3·90	3190	1·89	This paper.
α-Cyperone	2510	4·28	3120	2·07	,,

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153. *The Oxidation of the Silicon Hydrides. Part II.*

By H. J. Emeléus and K. Stewart.

We have already shown (J., 1935, 1182) that the oxidation of monosilane is a typical chain reaction, exhibiting the phenomena of a lower and an upper critical explosion limit, and a quantitative study was made of the effects of mixture composition, dimensions of the reaction vessel, and diluent gases on the lower limit, and of mixture composition, temperature, diluent gases, and inhibiting substances on the upper limit. The experiments described below include the examination of the effect of temperature on the lower limit for the oxidation of monosilane, and also of the ignition phenomena exhibited by disilane and trisilane, both of which were found to resemble monosilane. Lower and upper explosion limits were observed and have been studied in some detail. Finally, an attempt has been made to correlate the data obtained for the three hydrides, Semenoff's generalised theory of chain rections being used as a basis.

Experimental.

Disilane and trisilane were isolated in a state of purity by the method of Stock and Somieski (*Ber.*, 1916, **49**, 111), the vapour pressures agreeing closely with the standard values. The apparatus employed previously in studying the lower critical explosion limit phenomena was modified so as to allow the silicon hydride and oxygen to enter the evacuated reaction vessel simultaneously through calibrated capillaries (Fig. 1). This ensures that the two gases mix thoroughly, and has the added advantage that it eliminates the use of the method of trial and error in determining the lower limit. The reaction vessel A was connected to the vacuum line by the standard ground joint G and the tap 7. The fine capillaries c_1 and c_2, the flow through which was determined for various pressures of the two gases by measurements with a McLeod gauge, were used to admit the silicon hydride and oxygen into A. The main reservoirs of these gases were connected to smaller auxiliary reservoirs, and the pressure in the latter was adjusted and measured, before each experiment. In measuring the lower limit, the apparatus was evacuated with taps 1, 2, 3, 4, 7, 8, and 9 open. Taps 1, 4, and 7 were then closed, and 5 and 6 opened. Simultaneously the stop-watch was started. After an interval of several minutes a glow appeared suddenly throughout A, but not in the quill connecting tubes. The pressures of the two reactants at the moment of ignition were calculated from the calibration data for the two capillaries.

The apparatus was then re-evacuated, and a fresh determination made, with different rates of flow of the two gases, after adjustment of the pressures in the auxiliary reservoirs.

The reaction vessel A was not coated with sulphuric acid as in the earlier experiments. Its inner surface was washed with a few c.c. of 50% hydrogen fluoride and rinsed with distilled water; it was surrounded by an electrically heated furnace of Pyrex glass and of 10 cm. internal dia-

meter. The temperature was constant to within $\pm 2°$. The volume of the dead space in the reaction system was not more than 4% of the volume of *A*.

The experimental method used in studying the upper critical explosion limit phenomena for disilane and trisilane was the same as that used for monosilane (*loc. cit.*).

Results.

Lower Critical Limits for Mono-, Di-, and Tri-silane.—The lower limit for monosilane was measured at 100°, the temperature previously used in studying its upper limit. The cylindrical reaction vessels had diameters 2·32, 3·04, and 4·86 cm., and were 20 cm. long. For disilane and trisilane the diameters were 1·30, 2·32, 3·04 cm. Measurements with the last substances were made at 0°. The surface of the reaction vessel was treated with hydrofluoric acid in each case, and was then allowed to become coated with a thin film of silica, which accumulated in successive experiments.

FIG. 1.

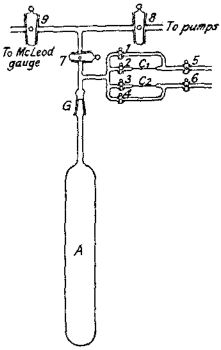
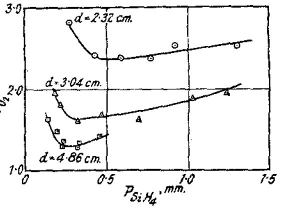


FIG. 2.



Effect of vessel diameter on lower limit for monosilane.

The curves shown in Figs. 2, 3, and 4 give the relation between the partial pressures of the silicon hydride and oxygen for reaction vessels of different diameters. The three sets of curves all show a lowering of the pressures as the diameter of the reaction vessel is increased. The critical pressures for silane–oxygen mixtures are of the order of 1·5—4 mm. For disilane–oxygen mixtures they are lower (0·1—1·0 mm.), and for oxidation of trisilane, which is generally regarded as spontaneously inflammable, the lower critical explosion limits lie at pressures of the order of 0·01—0·1 mm. In spite of the low magnitudes of these pressures, the experiments were strikingly reproducible. Over the pressure ranges shown in the diagrams the ignition was very sharply defined. Mixtures containing more than 50% of disilane gave a feeble glow, which became increasingly difficult to detect as the proportion of hydride was increased. The inflammation curves for trisilane are very steep, but the phenomena may be examined readily up to a point where the mixture contains 75% of hydride. The form of the curve for monosilane (Fig. 2) is somewhat unusual in that it shows a minimum, but this is adequately accounted for in the discussion of the reaction mechanism.

The general theory of chain reactions requires that the relationship $p_K{}^2 . d^2 . f(x) =$ const. should hold at the lower critical oxidation limit when studied in tubes of different diameter. In this equation, p_K is the lower critical pressure, d the diameter of the reaction vessel, and x the proportion of hydride in the gas mixture. If x is constant, and d is varied, the value of $p_K d$ should be constant. In Table I, values of the product $p_K d$ are given for each of the three hydrides.

The constancy of the product $p_K d$ for any given reaction mixture in tubes of various diameters is very satisfactory, particularly with disilane. When the value of p_K is plotted against x for a given value of d, the curve obtained shows a minimum at $x = 0·15$ for monosilane and at $x = 0·50$ for disilane. For trisilane no minimum was observed up to $x = 0·70$. The significance of this minimum in relation to the reaction mechanism is discussed on p. 682.

TABLE I.

SiH_4 (100°).

x.	p_Kd. d = 2·32.	3·04.	4·86.
0·10	6·95	6·25	8·07
0·15	6·62	5·80	7·45
0·20	6·86	6·17	8·00
0·25	7·40	6·94	9·30
0·30	8·21	7·79	—
0·40	—	10·45	—

Si_2H_6 (0°).

x.	p_Kd. d = 1·30.	2·32.	3·04.
0·10	0·768	0·836	0·755
0·20	0·494	0·551	0·425
0·30	0·423	0·429	0·380
0·35	0·396	0·404	0·371
0·40	0·385	0·385	0·371
0·45	0·380	0·377	0·377
0·50	0·388	0·366	0·377

Si_3H_8 (0°).

x.	p_Kd. d = 1·30.	2·32.	3·04.
0·10	—	0·116	0·111
0·20	0·100	0·079	0·082
0·30	0·069	0·061	0·063
0·40	0·055	0·050	0·050
0·50	0·047	0·042	0·043
0·60	0·043	0·037	0·038
0·70	0·039	—	—

The above values of p_K for monosilane are considerably higher than those obtained with tubes coated on the inside with concentrated sulphuric acid. This fact must be attributed to the different capacities of the two surfaces for breaking chains, the sulphuric acid surface being less efficient. Dissolution of either gas in the sulphuric acid, or contamination of the reactants by the acid, would tend to raise the lower limit. Glass surfaces which were washed only with distilled water gave higher values for p_K, but they were very erratic.

Effect of Temperature on the Lower Limits.—The lower critical explosion pressure of monosilane was found to increase with the temperature, an anomaly traced to a slow reaction taking place below the limiting pressure; this reaction was imperceptible at 100°. For instance, when the addition of monosilane and oxygen through the capillary leaks was interrupted for periods of ½—1½ hours, ignition took place at the same pressure (within 5%) as when the gases flowed into the reaction vessel without interruption. At 145° and 200° a similar interuption in the addition of gas increased the apparent critical pressure. Results of such experiments are shown in Table II. The proportiou of silane in the gas mixture is given in col. 2; col. 3 gives the fraction of the total gas added before the experiment was interrupted, col. 4 the period for which the experiments was interrupted, and col. 7 the percentage increase in the values of p_K.

TABLE II.

Temp.	SiH_4, %.	Fraction before interval.	Time interval (mins.).	p_K (obs.) (mm.).	p_K (continuous flow) (mm.).	Increase, %.
100° d = 4·86 cm.	12·3	0·83	45	1·52	1·57	—
	15·6	0·64	120	1·55	1·53	—
145° d = 3·04 cm.	18·1	0·38	10	3·57	3·06	14
	17·2	0·60	10	3·67	3·04	17
	10·7	0·41	10	3·69	3·12	15
193° d = 3·04 cm.	19·3	0·30	6	4·88	3·45	41
	20·3	0·36	6	5·36	3·60	49
	19·7	0·68	6	4·53	3·50	29
	17·4	0·42	60	4·20	3·20	31
	13·9	0·64	45	4·60	3·20	44

The effect of temperature on the lower limit for disilaue is apparently normal. Results obtained at 0°, 100°, and 193° are shown in Table III (data from smoothed curves). The limiting pressure falls with increase in temperature. This does not mean that there was no slow reaction below the lower limit, but rather that it was insufficient at the very low pressures used to produce the anomalous results found with monosilane. This would indicate that any reaction below the lower critical explosion limit is a surface reaction. Tests were made in the case of the measurements at 0° to determine the effect of interrupting the addition of the reacting gases, but the change in the lower limit was inappreciable for times of interruption up to 1 hour.

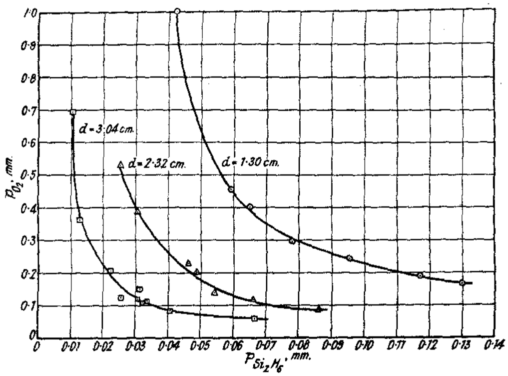
TABLE III.

Effect of temperature on p_K *for* Si_2H_6 (d = 3·04 cm.).

SiH_4, %. Temp.	10	20	30 (p_K (mm.))	40	50
0°	0·220	0·147	0·126	0·122	—
100	0·160	0·101	0·079	0·067	0·062
193	0·134	0·084	0·063	0·050	0·045

Upper Critical Explosion Limits of Disilane and Trisilane.—The upper limit phenomena for these two hydrides were studied at 0°. It was found possible to use the same method as for monosilane (Emeléus and Stewart, *loc. cit.*). Either hydride could be mixed with oxygen at

FIG. 3.



Effect of vessel diameter on lower limit for disilane.

total pressures of 40—70 cm., provided that the percentage of hydride in the mixture was low. Great care was needed, however, in mixing the gases, and it was necessary to evaporate the silicon hydride very slowly into the oxygen atmosphere after the two gases had been introduced into the

FIG. 4.

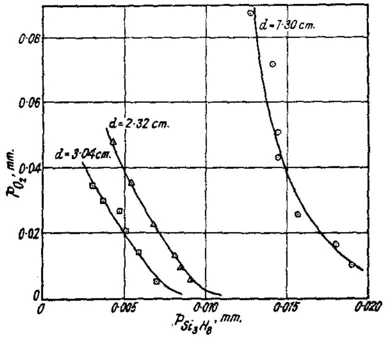
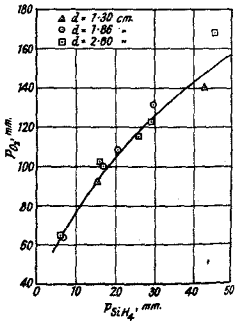


FIG. 5.



Effect of vessel diameter on lower limit for trisilane.

reaction vessel. If bumping of the liquid hydride occurred, the mixture exploded, owing to local enrichment of the gas mixture in hydride. This risk was particularly great with trisilane, and only a limited number of experiments on its upper critical explosion limit were successful.

The upper limit phenomena for disilane resemble those for monosilane; the diameter of the

reaction vessel had no appreciable effect on the limit. The results are shown in Fig. 5, in which readings with reaction tubes of diameter 1·30, 1·86, and 2·80 cm. are included. The experiments were carried out at 0°. The relation between the pressures of the reactants in the limit mixture is

$$[O_2] + 0{\cdot}81[Si_2H_6] = 625[Si_2H_6]/[O_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

This equation is used in the discussion in deducing certain constants for the reaction. The value of the upper critical pressure increases steadily with increasing concentrations of disilane. This was also an outstanding characteristic of the oxidation of monosilane at 100° (Emeléus and Stewart, *loc. cit.*).

Increase in temperature raised the value of the critical pressure, as shown by the data in Table IV, obtained with mixtures containing 10% of disilane. The values p_K (calc.) are those calculated from the general equation for inflammation based on the theory of chain reactions (p. 683).

TABLE IV.

Temp.	0°	16·5°	30·0°	36·0°	44·5°
p_K (obs.)	70·5	119	145	153	186
p_K (calc.)	70·5	105	139	156	182

The magnitudes of these critical pressures for disilane at 0° are of the same order as those of monosilane at 100°. To some extent this is a manifestation of the increase in " inflammability " of the silicon hydrides as the homologous series is ascended.

The effect of small concentrations of ethylene on the upper limit for disilane at 0° was studied with a constant ratio (0·25) of disilane to oxygen. The results are tabulated below, and it will be seen that the ethylene acts as an inhibitor of the explosion, its effect being very similar to that on the oxidation of monosilane: no doubt a great number of typical inhibitors of oxidation reactions would act similarly.

p_K (mm.)	167	133	107	100	77	65
$p_{C_2H_4}/p_{O_2} \times 10^2$	0	0·17	0·31	0·63	1·15	2·0

The few observations made on the upper limit of trisilane at 0° are given below. The proportion of hydride must be very low for it to be possible to obtain a mixture with oxygen. Nevertheless, such a mixture can be obtained, and explodes when the total pressure is reduced. The values tabulated under p_K (calc.) were calculated from the equation given on p. 683.

A more extensive study of the critical oxidation phenomena of trisilane would be possible if the experiments could be conducted at a lower temperature. A limit would, however, be set by the vapour pressures of the liquid hydride.

TABLE V.

Si_3H_8/O_2	0·0145	0·0124	0·0107
p_K (calc.), mm.	281	240	207
p_K (obs.), mm.	252	223	255

DISCUSSION.

The following mechanism for the oxidation of monosilane was suggested by the authors (*loc. cit.*):

$$SiH_4 + O = SiH_2 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$SiH_2 + O_2 = SiH_2O + O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$SiH_2O \longrightarrow \overset{O_2}{\ldots\ldots} \longrightarrow SiO_2 \quad . \quad \text{(degenerate branching)}$$
$$O^* + O_2 = O + O_2^* \quad . \quad . \quad . \quad . \quad \text{(energy branching)}$$
$$O + O_2 + M = O_3 + M \quad . \quad \text{(gas-phase deactivation)}$$
$$O \text{ or } SiH_2 + \text{wall} \quad . \quad . \quad . \quad . \quad \text{(surface deactivation)}$$

If q_1 and q_2 collisions are necessary for reactions (1) and (2) respectively to take place, the general equation defining the upper and lower critical explosion pressures as the proportions of the reactants are changed is

$$1 + \varepsilon\frac{q_1}{\delta}\frac{[O_2]}{[SiH_4]} = \left(\frac{z_3}{z_2}\mu\right)\cdot\frac{q_1}{\delta}\frac{[O_2]}{[SiH_4]}\{[O_2]+[SiH_4]\} + 3{\cdot}65\frac{\lambda_0^2}{d^2}\frac{\frac{q_1}{\delta}[O_2] + \frac{q_2}{\delta}[SiH_4]}{[O_2][SiH_4]\{[O_2]+[SiH_4]\}} \quad . \quad (3)$$

where pz_3/z_2 is the ratio of triple to double collisions at the pressure p, which equals to the sum of $[O_2] + [SiH_4]$; ε, δ, and μ are respectively the probabilities of reaction in a collision between atomic and molecular oxygen, of branching at any given link, and of gas-phase deactivation, λ_0 *is the mean free path at 1 mm. pressure and* d *is the diameter of the* reaction vessel. If this equation is first applied to the lower-limit data, deactivation by triple collisions (represented by the first term on the right-hand side) may be neglected. The value $\varepsilon q_1/\delta = 0{\cdot}202$, previously found from the limit for silane at 100°, may be inserted.

Further, we may put $[O_2] = (1 - x)p_K$ and $[SiH_4] = xp_K$, where x is the proportion of monosilane in the reaction mixture, and p_K is the lower critical oxidation limit at 100°. Equation (3) then reduces to

$$p_K^2\left\{1 + 0{\cdot}202\left(\frac{1-x}{x}\right)\right\} = \frac{3{\cdot}65\lambda_0^2}{d^2}\left\{\frac{q_1}{\delta}\cdot\frac{1}{x} + \frac{q_2}{\delta}\cdot\frac{1}{1-x}\right\} \quad . \quad . \quad . \quad (4)$$

When the experimental values of p_K for silane (Table I) are plotted against x a minimum is found at $x = 0{\cdot}15$. This minimum value can be applied to obtain a value of the ratio q_2/q_1 by differentiating equation (4) and inserting in the resulting expression the value $x = 0{\cdot}15$. It is thus found that $q_2/q_1 = 2{\cdot}61$, *i.e.*, 2·61 times as many collisions between a SiH_2 radical and molecular oxygen are needed for reaction as in the reaction of atomic oxygen and monosilane. The values of q_1/δ and q_2/δ derived therefrom are $1{\cdot}52 \times 10^5$ and $3{\cdot}96 \times 10^5$; also, $(z_3/z_2)\mu = 1{\cdot}51 \times 10^{-8}$ and $\varepsilon = 1{\cdot}33 \times 10^{-6}$.

The values of q_1 and q_2 are inseparable from δ, the probability of branching. It is considered probable, however, that δ will vary exponentially with temperature, in which case q/δ can be written in the form $e^{E/RT}$.

This form is used in discussing the results for disilane below, where the effect of temperature on the upper critical oxidation limit has to be considered.

Oxidation of Disilane.—The kinetics of the oxidation of disilane may be represented by a reaction scheme similar to that for monosilane. The active centre which initiates the reaction is assumed to be atomic oxygen. Thus:

$$Si_2H_6 + O = Si_2H_4 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$Si_2H_4 + O_2 = Si_2H_4O + O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$Si_2H_4O \longrightarrow \overset{O_2}{\ldots\ldots} \longrightarrow SiO_2 \quad . \quad . \quad \text{(degenerate branching)}$$

$$O + O_2 + M \longrightarrow O_3 + M \quad . \quad . \quad . \quad \text{(gas-phase deactivation)}$$

$$O \text{ or } Si_2H_4 + \text{wall} \longrightarrow \text{surface deactivation.}$$

If q_1 and q_2 have the same meaning as before with reference to equations (5) and (6) respectively, and if $q_1/\delta = e^{E_1/RT}$ and $q_2/\delta = e^{E_2/RT}$, the complete equation for inflammation is

$$\left(\frac{z_3}{z_2}\right) e^{E_1/RT}\frac{[O_2]}{[Si_2H_6]}\{\mu_1[O_2] + \mu_2[Si_2H_6]\} + 3{\cdot}65\frac{\lambda_0^2}{d^2}\frac{e^{E_1/RT}[O_2] + e^{E_2/RT}[Si_2H_6]}{[O_2][Si_2H_6]\{[O_2] + [Si_2H_6]\}} = 1 \quad . \quad (7)$$

At the lower limit, deactivation by triple collisions, represented by the first term in equation (7), is neglected. It is then found, by the method used for monosilane, that $q_1 = q_2$. This is inherent in the data in Table I, where the minimum in the relationship between p_K and x is shown to occur at approximately $x = 0{\cdot}5$. It is also found that $q_1\delta = q_2/\delta = 900 = e^{3700/RT}$ (for $T = 273°$).

The effect of temperature on the lower-limit phenomena is represented by the equation

$$\log_{10} p_K/T = \bar{E}/2{\cdot}3RT + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This equation was developed by Semenoff and allows for the loss of heat from the gas. It replaces the equation $\log p = \bar{E}/RT + B'$, and the constant $\bar{E} = E/2$. Insertion of experimental values of the lower limit of disilane into equation (8) gives a value of $\bar{E} = 1830$ g.-cals., *i.e.*, $E = 3660$ g.-cals. This value of E is in good agreement with the value, 3700, calculated from equation (7).

At the upper limit, wall deactivation is neglected and equation (7) reduces to the same form as the experimental equation [(a), p. 681]. By comparing the constants of these two equations, and inserting the value $q/\delta = 900$ deduced from the lower-limit data, it is found that $\mu z_3/z = 1{\cdot}78 \times 10^{-6}$ and $\mu_2/\mu_1 = 0{\cdot}81$.

In equation (7) the term $e^{E/RT}$ ($= q/\delta$) governs the influence of temperature, and it is possible to use the value $q/\delta = 900$, deduced from the lower limit, to predict the temperature variation of the upper limit of disilane. Values calculated in this way are included in Table IV and agree well with the experiment.

The lower-limit results for trisilane show no minimum in the plot of p_K against x for values of x up to 0·75, though a minimum must occur for still higher values. The mechanism of the oxidation of trisilane is probably similar to those for mono- and di-silane, two active centres being required for chain propagation, one of which is the oxygen atom. If, as before, q_1 and q_2 collisions are needed for these two reactions to take place, q_1 and q_2 may be taken as equal to a first approximation. It can then be shown on the experimental data on the lower limit for trisilane that $q/\delta = 30$, corresponding with a very low energy of activation. This approximation enables us to predict the values of the upper limit of trisilane. If the value $\mu z_3/z_2 = 1{\cdot}78 \times 10^{-6}$ found for the oxidation of disilane is inserted, the equation for the *upper* critical limit, derived in the same manner as for disilane, is $p_K = 1{\cdot}94 \times 10^4[Si_3H_8]/[O_2]$. Values of p_K calculated from this relationship are shown in Table V, and it is seen that the agreement is better than would be expected from the assumptions made.

The results of Schantarowitsch on the oxidation of monosilane (*Acta Physicochim. U.R.S.S.*, 1935, **2**, 633) lead to the same general conclusions as the experiments described in this paper. There is, however, one outstanding discrepancy. Our monosilane was decidedly more readily inflammable than that used by Schantarowitsch: it gave lower values for the lower limit, and lower values for the minimum ignition temperature of a given mixture. The vapour-pressure measurements of our material agreed with the values published by Stock and Somieski (*loc. cit.*). Reaction with alkali gave exactly the theoretical amount of hydrogen. Finally, the absorption spectrum, which was examined in connection with work in progress on the photodecomposition and oxidation of these hydrides, also afforded no evidence of appreciable contamination by higher hydrides. Schantarowitsch prepared monosilane from silicochloroform, and showed that the product after fractionation gave the theoretical volume of hydrogen when treated with alkali. In these circumstances the discrepancy between the two sets of results must be due either to a trace of more inflammable hydride in our material, to a trace of inhibiting substance in Schantarowitsch's, or to differences in the surface conditions in the two sets of experiments.

The lower critical oxidation for monosilane has been studied recently by Gutschmidt and Clusius (*Z. physikal. Chem.*, 1935, *B*, **30**, 265), who compressed the gas mixtures by allowing mercury to flow into the reaction vessel. In our experience this method does not readily yield reproducible results: a luminescence is sometimes observed at the surface of the moving mercury meniscus before the limiting pressure is reached.

Norrish's mechanism (*Proc. Roy. Soc.*, 1935, *A*, **150**, 36) for the oxidation of methane is essentially of the same type as that developed independently by the authors to account for the chain oxidation of monosilane. It was shown by Schantarowitsch (*loc. cit.*) that the explosive oxidation of monosilane occurs at a lower temperature if a trace of nitrogen dioxide is added. This experiment finds its counterpart in the sensitisation of methane explosion by nitrogen dioxide. The main points of difference between oxidation of hydrocarbons and of silicon hydrides are (i) that the latter ignite at much lower temperatures, and (ii) that the transition from the slow oxidation to explosion is far more rapid in the case of the silicon hydrides. The work is being extended with the object of elucidating these points of difference.

Summary.

(1) The lower critical explosion pressures of mono-, di-, and tri-silane in dry glass reaction vessels have been studied.

(2) The upper critical explosion pressures of the last two have been studied.

(3) The effect of increase of temperature on these limits is to diminish the lower pressure limit and to raise the upper limit.

(4) The three hydrides form a graded series, in which the inflammability increases with the molecular weight.

(5) The results have been analysed on the theory of chain reactions, and certain conclusions deduced.

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IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, March 11th, 1936.*]

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154. *Mutually Surface-active Liquids. Mixtures of Sulphuric Acid with Nitrobenzene and with Ether.*

By KENNETH CLAUDE BAILEY.

WHEN the surface tensions of a series of mixtures of two liquids are plotted against percentage composition, the curve obtained usually shows neither a maximum nor a minimum surface tension. In a small proportion of the cases examined, mixtures have been found with surface tensions higher, or lower, than that of either pure component. The following examples are on record, but the list is not exhaustive.

[The figures in parentheses give the surface tensions (dynes/cm.) of the component liquids and of the maximum or minimum mixtures.]

Maximum surface tensions. Methyl alcohol (21·058) and acetone (21·578): 33% methyl alcohol (21·775) (at 30°) (Morgan and Scarlett, *J. Amer. Chem. Soc.*, 1917, **39**, 2276). Ethyl alcohol (19·589) and acetone (19·781): 50% ethyl alcohol (19·831) (at 45°) (Morgan and Scarlett, *loc. cit.*, who observed no maximum at 20° or at 0°). Sulphuric acid (53·66, 98·7% acid) and water (72·82): 47·58% acid (76·70) (at 18°) (Röntgen and Schneider, *Wied. Ann.*, 1886, **29**, 209; Whatmough, *Z. physikal. Chem.*, 1902, **39**, 129, records a maximum at 45% sulphuric acid). *p*-Cresol (0·437*) and acetone (0·315*): 21% acetone (0·450*). *m*-Cresol and acetone: slight maximum at 21% acetone. *o*-Cresol and acetone: no maximum (Weissenberger and others, I.C.T., VII, p. 70; from *Monatsh.*, 1925, **45**, 449; **46**, 1, 47).

Minimum surface tensions. Carbon disulphide (32·24) and ethylene dichloride (32·66): 50% carbon disulphide (30·63) (at 18°) (Whatmough, *loc. cit.*, p. 169). Acetic acid (28·08) and ethyl iodide (28·83): 40% ethyl iodide (26·69) (at 18°) (*ibid.*, p. 170). Acetic acid (28·08) and carbon tetrachloride (27·05): 50% acetic acid (26·26) (at 18°) (*ibid.*). Acetic acid (28·00) and benzene (28·94): 50% benzene (27·68) (at 18°) (*ibid.*, p. 171). Acetic acid (25·71) and benzene (26·62): 62·9% acetic acid (24·96) (at 30°) (Morgan and Scarlett, *loc. cit.*). Acetic acid (27·17) and benzene (28·55): 65·2% acetic acid (26·71) (at 15°) (*idem*). Acetic acid (28·00) and chloroform (27·40): 40% chloroform (26·62) (at 18°) (Whatmough, *loc. cit.*, p. 172). Carbon tetrachloride (27·00) and chloroform (27·33): 45% chloroform (26·92) (at 18°) (*idem*). Ethyl acetate (24·22) and amyl alcohol (24·29): 68% amyl alcohol (24·13) (at 18°) (*idem*). Benzene (28·94) and ethyl iodide (28·83): 50% ethyl iodide (28·61) (at 18°) (*idem*). Benzene (25·36) and toluene (25·29): 25% benzene (25·21) (at 40°) (Morgan and Griggs, *J. Amer. Chem. Soc.*, 1917, **39**, 2265; they did not observe a minimum at 10·8°, nor did Whatmough at 18·0°).

It is noticeable, although perhaps merely a coincidence, that in all the cases of minimum surface tension, the surface tensions of the components are nearly identical, the greatest difference being 1·38 dyne/cm. (acetic acid and benzene at 15°).

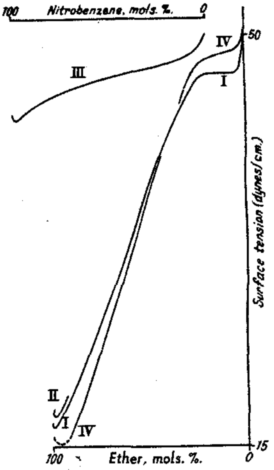
In the course of other work, it was desired to determine the surface tensions of dilute solutions of (*a*) nitrobenzene and (*b*) ether in sulphuric acid (100%). It was decided to

* Surface tension relative to that of water.

extend the series of measurements over the whole range of these mixtures, and it was found that both curves showed minimum points. These cases differ from the above in that the surface tension of sulphuric acid differs widely from those of the other components, being about 7 dynes/cm. higher than that of nitrobenzene, and about three times that of ether.

The surface tensions of mixtures of ether and sulphuric acid were determined by Pound (J., 1911, **99**, 709), who observed no minimum at 30°; however, he made no measurements between 0 and 10·94% sulphuric acid, and a comparison between the curve drawn from his results and that now obtained makes it almost certain that a minimum (as indicated by the broken line) would have been detected at 30° also if the appropriate measurements had been made.

The fall in surface tension at each end of each curve makes it clear that sulphuric acid, in small concentration, in spite of its high surface tension, is positively adsorbed at the surface of ether or nitrobenzene, and that these two substances are adsorbed, in similar circumstances, at the surface of sulphuric acid.



Experimental.

Materials.—The sulphuric acid was purified by repeated crystallisation, and adjusted to 100% by small additions of pyrosulphuric acid similarly recrystallised. The 100% acid (concentration checked by m. p. and by titration) was kept in a desiccator in a very dry constant-temperature room. It was found, by repeated checking, that the rate of acquisition of water was exceedingly small.

The ether and nitrobenzene were purified by repeated distillation of specimens which were already practically pure.

Method.—Measurements were made by the drop-weight method, the stalagmometer previously employed by Hickson and Bailey (*Sci. Proc. Roy. Dublin Soc.*, 1932, **20**, 274) being used in conjunction with the device recently described by the author (*Nature*, 1936, **137**, 323) for controlling the rate of fall of the drop. The values of $f(r/l)$ in the equation $\gamma = Wg/2\pi r \, . \, f(r/l)$ were taken from the paper by Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499).

Most of the readings were taken in a constant-temperature room at 17°. To minimise error due to evaporation in the case of ether-rich mixtures, the weight of the first five drops was neglected, and the later drops fell in an atmosphere already saturated with ether vapour. As, however, some inaccuracy is likely to be introduced at a temperature so near the b. p. of ether, a further set of measurements of ether-rich mixtures was made at 9·5° (Table I). These left no doubt about the genuineness of the fall in surface tension when a little sulphuric acid is added to ether.

Table I.

Sulphuric acid and ether at 9·5°.

Ether, mols. % ...	94·13	97·69	98·43	98·77	99·24	99·38	99·49	100·0	100·0
γ (dynes/cm.)	18·90	17·82	17·84	17·48	17·58	17·88	17·96	18·12	18·16

The number of readings taken was considerable, particular attention being paid to the extreme ends of the curves. In the figure, curves I and II represent sulphuric acid–ether mixtures at 17° and 9·5° respectively, and curve III sulphuric acid–nitrobenzene mixtures at 17°. Curve IV is drawn from Pound's results (*loc. cit.*) with the necessary alterations from percentages by weight to molecular percentages.

From these curves, the values in Table II are read off as the most probable surface tensions.

TABLE II.

Mixtures of sulphuric acid with ether or nitrobenzene.

H_2SO_4, mols. %.	Ether at 17°.	Nitro-benzene at 17°.	H_2SO_4, mols. %.	Ether at 17°.	Nitro-benzene at 17°.	H_2SO_4, mols. %.	Ether at 17°.	Nitro-benzene at 17°.	Ether at 9·5°.
100	50·33	50·33	90	48·83	48·25	5	17·97	43·10	18·63
99·5	49·40	50·05	80	46·80	47·76	4	17·60	42·80	18·31
99·0	48·75	49·83	75	46·30	47·52	3	17·30	42·73	17·99
98·5	48·24	49·66	60	41·60	46·87	2	17·06	42·85	17·67
98·0	47·83	49·54	40	32·50	46·05	1·5	16·90	42·98	17·53
97·0	47·22	49·25	20	23·30	44·80	1·0	16·80	43·11	17·51
96·0	46·93	49·00	10	19·55	43·98	0·5	16·80	43·27	17·78
95·0	46·86	48·80	7	18·50	43·64	0	17·06	43·47	18·13

TRINITY COLLEGE, DUBLIN. [*Received, March 21st, 1936.*]

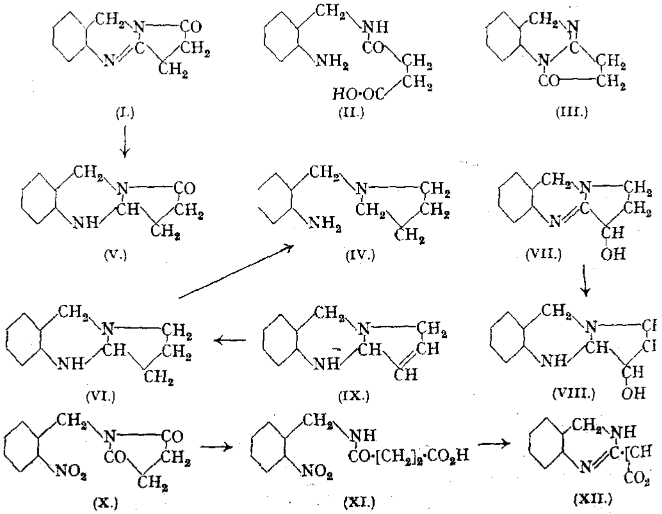
155. *The Electrolytic Reduction of Vasicine.*

By KARTAR S. NARANG and JNANENDRA N. RAY.

SPÄTH and PLATZER (*Ber.*, 1936, **69**, 387) have been unable to support the following results and conclusions reached by Juneja and us (J., 1935, 1277):

(a) (I) on electrolytic reduction gave a base $C_{11}H_{16}N_2$, instead of $C_{11}H_{14}N_2$ found by us, which they consider to be 1-*o*-aminobenzylpyrrolidine (IV), m. p. 30—31°. Therefore the conclusion of Juneja, Narang, and Ray that vasicine (VII) has a linear cyclic formula is considered to be based on unsound experimental evidence.

(b) Juneja, Narang, and Ray obtained a substance (III) by the ring closure of the substance (II), whereas Späth and Platzer find that the substance (I) is formed, because a mixture of the two substances shows no lowering in m. p.



We have reinvestigated (*a*) and find that the electrolytic reduction of vasicine (VII) proceeds through four distinct stages: (1) reduction of N=C in the middle ring (V from I and VIII from VII); (2) formation of an unsaturated substance by the loss of water from the oxygenated part in the third ring (IX from VIII); (3) reduction of the unsaturation temporarily created in (2) to (VI); (4) disruption of the middle ring (IV).

In an experiment on the reduction of (I) as described (J., 1935, 1277), the time of reduction was diminished to 5 hours. After isolation in the usual manner the *base* (V), was obtained, m. p. 115° after crystallisation from light petroleum (Found: C, 70·2; H, 6·4. $C_{11}H_{12}ON_2$ requires C, 70·2; H, 6·4%). It contained no amino-group (shown by the diazo-reaction). Vasicine was similarly reduced for five hours and the *picrolonate* of the reduction product (VIII) was isolated; purified by recrystallisation from hot alcohol, it formed parallelepiped plates, m. p. 165—168° (decomp.) (Found: N, 19·6. $C_{11}H_{14}ON_2,2C_{10}H_8O_5N_4$ requires N, 19·5%). This substance also contained no diazotisable amino-group. Therefore, whether vasicine or (I) is reduced, the first addition of hydrogen takes place at N=C in the middle ring. Again, reduction of a sample of vasicine was continued for 8 hours and then interrupted for ½ hour; the current was re-established for 15 minutes, but inadvertently the poles were reversed. This error was rectified, and reduction carried on for another 2 hours. The *base* (IX) isolated was converted into its *picrolonate*, which formed needles, m. p. 224—228° (decomp.) after crystallisation from alcohol (Found: C, 57·7; H, 4·7; N, 19·0. $C_{11}H_{12}N_2,C_{10}H_8O_5N_4$ requires C, 57·8; H, 4·5; N, 19·2%). The base isolated from the picrolonate had m. p. 92° and crystallised from ligroin in needles (about 1 cm. long) (Found: N, 15·8. $C_{11}H_{12}N_2$ requires N, 16·2%); the available material was insufficient for recrystallisation.

The base from the picrolonate of (VI) (J., 1935, 1279) was isolated; it melted at *ca.* 65° without crystallisation [Späth and Platzer give m. p. 30—31° for the base (IV)]. After being submitted to the process of diazotisation it did not give an azo-colour with alkaline β-naphthol solution. The base was not sufficient in amount for recrystallisation and analysis. We considered it hardly necessary to analyse the base, as the full analysis of its picrolonate has already been recorded.

Lastly, in an experiment in which vasicine was reduced for 21 hours, we got a base which gave an unmistakable diazo-reaction but could not be satisfactorily purified. This was 1-*o*-aminobenzylpyrrolidine (IV) formed by disruption of the middle ring and probably is the substance isolated by Späth and Platzer. From the mother-liquor of the crystallisation of the picrolonate of (VI), there was occasionally deposited a small amount of a second substance of approximately the same m. p. (204—207°) but differing in crystalline form. This substance markedly depressed the m. p. of the picrolonate of (VI) and the base from it gave a diazo-reaction. A space model reveals some strain in the middle ring and it is conceivable that this opens during vigorous reduction.

The reduction of vasicine therefore proceeds through (VII) ⟶ (VIII) ⟶ (IX) ⟶ (VI) ⟶ (IV). We have now demonstrated the stages (VIII) and (IX). Späth and Platzer have shown the stage (IV). Therefore the reduction must have passed through the stage (VI), which we have already described and no purpose would be served in recapitulating the details. In all the experiments the reduction was carried out continuously for 8 hours, stopped for 12 hours, and then resumed for the requisite time. In the reduction of vasicine or (I), 15—16 hours was sufficient for the stage (VI). Lastly, by a different method from ours, Späth and Platzer prepared a picrolonate of (VI) for which they give m. p. 195—197°; we recorded m. p. 202°, but we now find that the m. p. depends on the rate of heating and is 195—197° with slow heating in a vacuum. This is sufficient confirmation of our statement that the product we described is (VI). The structure is not disproved because a further product is obtainable on more vigorous reduction. Thus the objection (*a*) is answered.

(*b*) We have again taken a mixed m. p. of our substance (III) and the substance (I) and find a depression of more than 60°; the mixture melts at 125—135°. The two products differ in solubility and in crystalline form, the one crystallising in long prismatic rods and the other in stellate clusters of minute needles. Moreover, the picrolonates of the electrolytic reduction product of (I) and of the reduction product of (III) crystallise in well-defined

rectangular plates and thick prisms respectively and a mixture of the two shows a considerable depression in m. p. We are certain that heating of *o*-aminobenzylsuccinamic acid (II) with sodium acetate results in the production of the angular cyclic product (III), as this is a strainless structure. Späth and Platzer have found that *o*-nitrobenzylsuccinamic acid on heating is converted into succino-*o*-nitrobenzylimide : this is no proof of the linear structure also being formed in the case of ring closure of (II).

A possible reason for Späth and Platzer's (I) and (III) being identical is this : since they isolate 3 : 4-dihydroquinazoline-2-β-propionic acid (XII) as a by-product, it is clear that this substance has been formed by ring-opening during reduction. The intermediate (XI) may undergo reduction to (II) and thence to (III), or (XII) itself may give (III) owing to the mobility of the amidine system. In this case the same product would be formed as in the ring closure of (II). The isolation of (XII) suggests that in the reduction Späth and Platzer may not have followed our conditions. We do not say that in every experiment this has happened, because their isolation of 1-*o*-aminobenzylpyrrolidine (IV) by electrolytic reduction indicates that the sample in that experiment at least had the linear structure (I), unless of course (I) in that case was prepared by their alternative method of cyclisation of succino-*o*-aminobenzylimide.

If it is admitted that the substance (I) is different from (III) in the manuer we suggest, then one and the same product cannot be obtained from (III) and (I) by electrolytic reduction. Even if the ring opens in the case of (I) as Späth and Platzer find, to form 1-*o*-aminobenzylpyrrolidine (IV), it is difficult to see how this substance can be formed fron (III) by ring opening. Therefore the whole of the argument of Späth and Platzer falls and no further comments on our part become necessary.

Späth and Platzer found the following discrepancies in melting points (ours are in parentheses) : (1) succino-*o*-nitrobenzylimide, m. p. 133° (after two distillations in high vacuum) (130°); (2) *o*-nitrobenzylsuccinamic acid, m. p. 123—124° (116°); (3) th substance (I), m.p. 191° (186°). In our hands, (1) gave the same m. p. as before, but (should be 126° instead of 116°. As regards (3), the substance which Späth and Platz consider to be (I) is in reality (III), for which we get the m. p. 192°. The m.p.'s record by us are uncorrected.

THE UNIVERSITY, LAHORE. [*Received, March 24th, 1936.*]

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156. *The Interaction of Alkyl Chlorosulphinates and Pyridine in Ethereal Solution.*

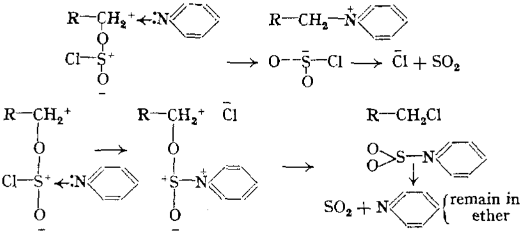
By WILLIAM GERRARD.

CONSIDERABLE interest attaches to the use of pyridine with thionyl chloride in effect the replacement of the alcoholic hydroxylic group by a chlorine atom (see Silberr *J. Soc. Chem. Ind.*, 1926, **45**, 37, 55; Clark and Streight, *Trans. Roy. Soc. Canada*, 19 **23**, III, 77), and the suggestion has been made by Kenyon, Lipscomb, and Phillips 1930, 415) that the pyridine not only facilitates the formation of the intermediate chl sulphinate, but also aids its decomposition into the chloride by forming an unst pyridinium chloride, $RO—\overset{+}{S}(O^-)—\overset{+}{N}—C_5H_5,\overset{-}{Cl}$. During a study of Walden inversion reacti involving the replacement of the hydroxyl group in ethyl *d*-lactate by a chlorine a (Gerrard, Kenyon, and Phillips, unpublished), it was observed that when ethyl *d*-α-chl sulphinoxypropionate was added to pyridine in cold ethereal solution, a pale yellov separated, leaving in the ether but a third of the theoretical yield of ethyl *d*-α-chloro pionate. From the analysis of the picrate yielded by the oil, the latter appeared to sist chiefly of a salt of 2-carbethoxypyridinium hydroxide. Furthermore, when a ch sulphinate, RO·SOCl, is added to an ethereal solution of an alcohol, R'OH, and pyri a precipitate of pyridine hydrochloride is produced, and an almost theoretical yield o sulphite, $RR'SO_3$, can be obtained from the ethereal solution (Voss and Blanke, *Ann*

1931, **485**, 258; Gerrard, Kenyon, and Phillips, *loc. cit.*). It appeared to be of interest, therefore, to examine the interaction of alkyl chlorosulphinates and pyridine itself in cold ethereal solution.

It is now shown that when the alkyl chlorosulphinate, RO·SOCl, is mixed with pyridine in cold dry ether, a yellow oily mixture of 1-alkylpyridinium chloride and 1-alkylpyridinium chlorosulphinate separates in quantity, leaving in the ether about a 40% yield of the alkyl chloride. With 1 mol. of the chlorosulphinate per mol. of pyridine, nearly a third of the base remained in the ether at the end of the reaction; but with 0·5 mol. of the base, no pyridine remained in the ether, and the yield of alkyl chloride was somewhat larger. The aqueous washings of the ethereal solutions at the end always contained a considerable amount of sulphur dioxide, but scarcely any chloride ion.

To account for these observations it is suggested that there are two distinct mechanisms by which pyridine reacts with the chlorosulphinate :



From a consideration of the arrangement of electrons in the chlorosulphinate molecule, it seems probable that there are two points where positive charges tend to polarise. It is conceivable that the lone pair of electrons on the nitrogen atom of the pyridine molecule could be accommodated at either of these points. If attachment took place at the carbonium point, the C—O link would be disturbed, and, following the scission indicated, the pyridinium cation would be formed. On the other hand, if attachment took place at the sulphur atom, the release of the chlorine anion might be followed by a scission at the C—O link resulting in the formation of the unstable complex, $SO_2NC_5H_5$, which decomposes into pyridine and sulphur dioxide. The re-formed pyridine is then available for further reaction by either of the two mechanisms proposed.

It is not likely that the alkylpyridinium compound is formed by the addition of the alkyl chloride to the unchanged pyridine; for this combination proceeds very slowly in ethereal solution at room temperature. *iso*Amyl chloride mixed with pyridine in dry ether gave no deposit after three months, even when the solution had been saturated with dry sulphur dioxide.

In contrast to chlorosulphinates, the chlorides of carboxylic acids do not give quaternary pyridinium compounds; *e.g.*, acetyl chloride and benzoyl chloride yield additive compounds with pyridine, but with water these decompose readily into dehydracetic acid and benzoic anhydride respectively (Minunni, *Gazzetta*, 1892, **22**, ii, 213; Wedekind, *Ber.*, 1901, **34**, 2070).

The isolation and identification of the alkylpyridinium compounds were effected in the first place by the precipitation from aqueous solution of their sparingly soluble *ferrocyanides*, $(C_5H_5NR)_2,H_2Fe(CN)_6,2H_2O$. At the dilution used, pyridine does not give a precipitate with potassium ferrocyanide (compare Cumming, J., 1922, **121**, 1287; 1923, **123**, 2457), so this affords an excellent means of separating the quaternary compounds from adventitious pyridine.

Experimental.

The chlorosulphinates were prepared as usual by adding the alcohol (1 mol.) slowly with vigorous shaking to freshly distilled, cooled thionyl chloride (1·3 mols.), keeping the product

in a desiccator for 4 hours, and distilling it at low pressure. The products were redistilled until pure and were used immediately.

General Procedure.—A solution of the appropriate chlorosulphinate in dry ether at $-10°$ was mixed with a cold solution of pyridine in dry ether, and the mixture was at once filtered rapidly from a small amount of white solid which always separated. The stoppered flask containing the filtrate was replaced in the freezing mixture and allowed to warm to room temperature. Within a few minutes after the mixing, there was an evolution of heat, and a pale yellow oil began to separate. At the end of 12 hours most of the oil had formed, but the deposition usually continued for a further 48—60 hours. The absence of chlorosulphinate at the end was indicated by the non-production of a white precipitate of pyridine hydrochloride on the addition of an alcohol (followed, if necessary, by pyridine) to a test portion of the ethereal solution.

The ether was decanted from the oil, washed successively with water, potassium carbonate solution, dilute hydrochloric acid, water, potassium carbonate solution, and finally dried over sodium sulphate prior to distillation through a 12-bulb column. From the residue thereby obtained, the alkyl chloride was isolated in the cases of *n*-butyl, *iso*amyl, and *iso*butyl chlorides. The aqueous extract of the ether contained a considerable amount of sulphur dioxide; but the first water and carbonate washings were practically free from chloride ion. When molecular proportions of the chlorosulphinate and pyridine had been used, the aqueous extract of the ether yielded on steam-distillation from alkaline solution about a third of the original quantity of pyridine, this estimation being effected by Schulze's method (*Ber.*, 1887, **20**, 3391).

The oils were miscible with water and alcohol in all proportions, sulphur dioxide being freely evolved on the addition of dilute mineral acid. When placed in a vacuum, the oils lost sulphur dioxide, rapidly at first, but retained some of it even after a month. The sulphur dioxide was estimated by distilling a weighed amount of oil from a solution of phosphoric acid in a stream of carbon dioxide, the distillate being absorbed in water kept slightly coloured with standard iodine solution added from a burette. Ionised chlorine was determined by the Volhard method. Very little pyridine, 0·5 g., was obtained when the oils were steam-distilled from alkaline solution, and the aqueous residues on acidification and treatment with potassium ferrocyanide solution gave the yellow ferrocyanides of the quaternary pyridinium compounds. These analyses indicated the oils to be mixtures of the alkylpyridinium chloride and chlorosulphinate.

The *alkylpyridinium ferrocyanides* were prepared by the slow addition of *N*-hydrochloric acid to an aqueous solution of the oil and potassium ferrocyanide. The yellowish crystalline precipitate was filtered off, washed well with water, and dried over calcium chloride in a desiccator. Oxidation frustrates attempts to obtain a further crop of crystals from the mother-liquor. Furthermore, if too much acid is added, a white precipitate is produced, and this appears to consist of $C_5H_5NR,H_3Fe(CN)_6,H_2O$.

In Table I are recorded the quantities of alkyl chlorosulphinate and pyridine used, together with the yields of oils and alkyl chlorides. Table II contains the data for the 1-alkylpyridinium ferrocyanides not previously described; and in Table III is recorded other evidence of the existence in the oils of 1-alkylpyridinium compounds, the data given being in accord with those

TABLE I.

Interaction of alkyl chlorosulphinates and pyridine.

RO·SOCl.					
R.	Wt., g.	C_5H_5N, g.	Vol. of Et_2O, c.c.	Yield of oil, %.	Yield of RCl, %.
CH_3	22·9	15·8	90	57·5	—
C_2H_5	25·7	15·8	60	72·2	—
,,	25·7	7·9 (0·5 mol.)	60	51·4	—
n-C_3H_7	28·5	15·8	70	76·6	—
n-C_4H_9	31·4	15·8	60	62·5	15·5
,,	31·4	7·9 (0·5 mol.)	60	45·8	49·7
iso-C_5H_{11}	17	7·9	40	52	32·9
,,	17	4 (0·5 mol.)	40	43·3	43·2
,,	17	2 (0·25 mol.)	40	17·3	47·9
iso-C_3H_7	28·5	15·8	70	61	—
iso-C_4H_9	31·3	15·8	70	55·8	23·2

published in the literature. For 1-methylpyridinium picrate, Ostermayer (*Ber.*, 1885, **18**, 592) gave the m. p. as 34°, whilst Decker and Kaufmann (*J. pr. Chem.*, 1911, **84**, 425) record m. p. 109—110° (needles) and m. p. 113—114° (rhombohedra); Kohn and Grauer (*Monatsh.*, 1913, **34**, 1751) give m. p. 107—110°.

The yields are calculated on the weight of chlorosulphinate, and the yields of oil are calculated on the weights of alkylpyridinium compound possible.

TABLE II.

1-*Alkylpyridinium ferrocyanides*, $(C_5H_5NR)_2,H_2Fe(CN)_6,2H_2O$, *obtained from the oils by addition of potassium ferrocyanide and hydrochloric acid solutions.*

R.	Yield, %.	Analyses, %.* C.	H.	N.	Fe.	Remarks.
Me	60·8	49·4	5·0	25·5	12·9	Orange-yellow; brown at 150°, does not melt.
		49·3	5·0	25·5	12·8	
				25·5	12·9	From 1-methylpyridinium iodide.
Et	74·8	51·3	5·5	24·0	12·0	Orange; brown at 143°; m. p. 150—151° (decomp.).
		51·5	5·4	24·0	12·0	
		51·3	5·5	24·0	12·2	From 1-ethylpyridinium iodide.
Pr	72·1			22·6	11·3	Orange-yellow; darkens at 140°, m. p. 143° (decomp.).
				22·7	11·3	
Bu	92·7	55·0	6·4	21·8	10·8	Chrome-yellow; turns brown at 163°, decomp. without melting at 165°.
		55·2	6·5	21·5	10·7	
iso-Amyl	94	56·7	6·9	20·3	10·2	Yellow.
		56·7	6·9	20·4	10·2	
iso-Propyl	—				11·4	Orange; decomp. 145°.
					11·3	
iso-Butyl	—				10·8	Yellow; decomp. 150°.
					10·7	

* The second line in each case gives the theoretical values.

TABLE III.

Derivatives of oils.

R.	Derivative.	Analyses.
Me	Picrate, m. p. 109°	N, 17·4 (Calc. for $C_{12}H_{10}N_4O_7$: N, 17·4%).
	Chloroaurate, m. p. 247°	
Et	Picrate, m. p. 89°	*N*, *16·8* (,, ,, $C_{13}H_{12}N_4O_7$: *N*, *16·7%*).
	Chloroaurate, m. p. 141—142°	
	Chloroplatinate, m. p. 201° (orange-red crystals)	
Pr	Chloroaurate, m. p. 128° (yellow crystals)	Au, 42·9 (,, ,, $C_8H_{12}NAuCl_4$: Au, 42·8%).
Bu	Chloroplatinate, m. p. 202°	*B*, 136·5 (,, ,, $C_5H_5N{\cdot}C_4H_9$: *B*, 136·0).
	Chloroaurate, m. p. 117°	
iso-Amyl	Chloroplatinate, m. p. 203°	*B*, 149·8 (,, ,, $C_5H_5N{\cdot}C_5H_{11}$: *B*, 150).
	Chloroaurate, m. p. 139°	
iso-Pr	Chloroaurate, m. p. 144°	Au, 42·7 (,, ,, $C_8H_{12}NAuCl_4$: Au, 42·8%).
iso-Bu	Chloroaurate, m. p. 139—140°	*B*, 138 (,, ,, $C_5H_5N{\cdot}C_4H_9$: *B*, 136).

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157. *Studies in the Toluene Series. Part V.* Sulphinic and Sulphonic Acids of the Mono- and Di-chlorotoluenes.*

By W. A. SILVESTER and W. PALMER WYNNE.

IN the course of their investigations of the isomeric mono- and di-chlorotoluenes, Wynne (J., 1892, **61**, 1042) and Wynne and Greeves (P., 1895, **11**, 151) converted these substances into their sulphonic acids for the purpose of characterising them. For the most part, the relative positions assumed by the SO_3H groups were not at that time ascertained, but since

* Earlier papers—Wynne, J., 1892, **61**, 1036, 1042; Wynne and Greeves, P., 1895, **11**, 151; Wynne and Bruce, J., 1898, **73**, 730.

such information might be expected to throw light on the comparative directing effect of the Cl and CH_3 radicals, it seemed desirable to continue the work, particularly as a parallel study had been made of the corresponding nitro-derivatives (Cohen and Dakin, J., 1902, **81**, 1334).

The methods employed were two in number: (i) Introduction of a second Cl atom into the molecule of a monochlorotoluenesulphonic acid of known constitution by nitration, reduction and the Sandmeyer reaction, and comparison of the dichlorotoluenesulphonic acid thus obtained with acids formed from dichlorotoluenes by direct sulphonation; (ii) replacement of the NH_2 radical in dichlorotoluidines of known constitution by the SO_2H group, which in Gattermann's process depends on the interaction of diazonium acid sulphites with copper powder, and oxidation of the sulphinic to sulphonic acids (*Ber.*, 1899, **32**, 1136).

By the first of these methods the constitution of the 2 : 5- and 3 : 4-dichlorotoluene-sulphonic acids was ascertained by Wynne and Greeves and by the second that of the remaining members in the course of the present investigation. In the table, in which the relative position of the SO_3H group in each acid is given, the constitution of the nitro-derivatives obtained by nitrating the dichlorotoluenes (Cohen and Dakin, *loc. cit.*) is also included for purposes of comparison.

Dichlorotoluene (Me in position 1).	Position of SO_3H.	M. p. of SO_2Cl.	M. p. of $SO_2{\cdot}NH_2$.	Position of NO_2 in nitro-derivative.
2 : 3	6 (89%)	51—52°	228°	6 (10%)
	5 (11%)	87	185	4 (90%)
2 : 4	5	72	176	5
2 : 5	4	43	191	4
2 : 6	3	60	204	3
3 : 4	6	82	189	6
3 : 5	2	45	168	2

These results are in general agreement with the course of substitution in benzene derivatives except in two noteworthy cases, the remarkable feature of which is the difference in position taken up by the entrant radical according as it is the SO_3H or the NO_2 group. Of these departures from uniformity the first is that recorded for 2 : 3-dichlorotoluene in the table; the second is exhibited by *p*-chlorotoluene, which when sulphonated gives as product a mixture of the 2-sulphonic acid (86%) with the 3-sulphonic acid (14%), but when nitrated, a mixture of the 2-nitro- (42%) with the 3-nitro-derivative (58%) (Wynne and Bruce, J., 1898, **73**, 733; Van der Arend, cf. Holleman, "Die direkte Einfuhrung von Substituenten in den Benzolkern," ed. 1910, p. 235).

In connexion with the synthesis of 2 : 6-dichlorotoluene-3-sulphonic acid from 2 : 6-dichloro-*m*-toluidine, opportunity was taken to investigate the chlorination of aceto-*m*-toluidide, which seemed to have received a less complete study than that of its *o*- and *p*-isomerides. Reverdin and Crépieux, using sodium chlorate and hydrochloric acid as the agent, isolated 6-chloro- and 4 : 6-dichloro-aceto-*m*-toluidide from the product (*Ber.* 1900, **33**, 2503), but both their description and that of later workers under other conditions suggest the presence of one or more isomerides. In our experiments, after it had been found that the passage of chlorine (1 mol.) into a solution of aceto-*m*-toluidide in glacial acetic acid gave in addition to mono-substituted products both 4 : 6- and 2 : 6-dichloro derivatives mixed with a noteworthy amount of unchanged toluidide, rendering the isolation of any one constituent difficult, it proved possible by the use of sulphuryl chloride to effect either mono- or di-substitution at will. Of the three monochloro-, the 6-, and of the two dichloro-, the 4 : 6- is the chief product.

Experimental.

*Monochlorination of Aceto-*m*-toluidide.*—For the production of 6-chloro-*m*-toluidine in the absence of more highly chlorinated compounds the best methods were found to be:

(i) Chlorination of aceto-*m*-toluidide in dilute aqueous solution (1 g. in 250 c.c.) with the calculated volume of chlorine water. After the lapse of a day the solution was extracted with chloroform, and the oily extract hydrolysed. From 34 g. of aceto-*m*-toluidide, 7 g. of 6-chloro-

m-toluidine, m. p. 85—86°, were obtained, the remainder of the product being mostly unchanged *m*-toluidine.

(ii) Chlorination with sulphuryl chloride (cf. Wynne, *loc. cit.*). In this preparation, sulphuryl chloride (1 pt.) was added to a solution of aceto-*m*-toluidide (1 pt.) in dry carbon disulphide (5 pts.) and, after removal of the solvent by distillation, the viscid residue which did not solidify was hydrolysed by hot hydrochloric acid. From the crystalline hydrochloride, which separated on cooling, almost pure 6-chloro-*m*-toluidine was obtained, but addition of alkali to the mother-liquor precipitated an oily mixture, the yield of chlorinated base being 98% of that calculated.

Cumulative fractional distillation separated from this oily mixture further quantities of 6-chloro-*m*-toluidine and a small amount of unchanged *m*-toluidine. The intervening fractions, b. p. 210—220°, 220—225° and 225—230°, when dissolved separately in 2*N*-sulphuric acid gave, on cooling, the remainder of the 6-chloro-compound as the comparatively insoluble sulphate. Re-acetylated, the oily bases separately regenerated from the soluble sulphates were fractionally extracted by cold alcohol, leaving a residue of 2-chloroaceto-*m*-toluidide, m. p. 132°, which on oxidation gave 2-chloro-3-acetamidobenzoic acid, m. p. 205°, whilst the more soluble constituent, m. p. 88—90°, proved to be 4-chloroaceto-*m*-toluidide, since in common with mixed acetyl derivatives remaining as a gummy mass after removal of the solvent, it was converted almost quantitatively into 4-chloro-3-acetamidobenzoic acid, m. p. 263°, on oxidation.

Three monochloro-derivatives therefore were produced under these conditions, the yields being approximately 80% of 6-chloro-, 12% of 4-chloro- and 8% of 2-chloro-aceto-*m*-toluidide.

Further chlorination of 6-chloroaceto-*m*-toluidide (5 pts.), dissolved in carbon disulphide, by sulphuryl chloride (4 pts.) gave a product from which after removal of the solvent the isomeric dichloroaceto-*m*-toluidides could not be separated by crystallisation and were therefore hydrolysed. Eventually a still imperfect separation of the bases was achieved by converting them into the sulphates and fractionally decomposing the mixture, suspended in water, by aqueous caustic soda. The fractions extracted by ether and recrystallised from light petroleum (b. p. 90—110°) gave 4 : 6-dichloro-*m*-toluidine, which separated in small hard prisms, m. p. 85°, from the more soluble 2 : 6-isomeride, m. p. 60°, in flat needles.

(I) *3-Chlorotoluene-sulphinic and -sulphonic Acid.*—(*a*) 3-Chlorotoluene-4-sulphinic acid was prepared by diazotising 3-chloro-*p*-toluidine (13 g.), b. p. 226—230°/759 mm., dissolved in sulphuric acid (30 g. in 100 c.c. of water) at 5—10°, adding more sulphuric acid (40 g. with 30 c.c. of water), and saturating the solution with sulphur dioxide (25 g.) at about 0°. A slow current of the gas being maintained, copper paste—obtained by decomposing copper sulphate solution with zinc dust—was stirred into the product until nitrogen was no longer evolved. The mixture, rendered alkaline with caustic soda, was filtered and excess of sulphuric acid added to the filtrate, whereupon the sulphinic acid partly separated as a flocculent mass, the remainder being extracted by ether. Recrystallised from this solvent, it formed silky needles, m. p. 110°, but decomposed somewhat readily. The *barium* salt, obtained by extracting the crude acid with hot baryta solution, crystallised in moderately soluble, radiating masses of thin scales [*Found*: Ba, 23·2; H_2O, 12·0. $(C_7H_6O_2ClS)_2Ba,4H_2O$ *requires* Ba, 23·3; H_2O, 12·2%].

Potassium 3-chlorotoluene-4-sulphonate, formed by oxidising the sulphinate with potassium permanganate, tended to give supersaturated solutions from which it separated in anhydrous irregular prisms (*Found*: K, 16·0. $C_7H_6O_3ClSK$ *requires* K, 16·0%). The *chloride* crystallised from ligroin in splendid rhombs, m. p. 46° (Found: Cl, 31·8. $C_7H_6O_2Cl_2S$ requires Cl, 31·6%), and the *amide* from aqueous alcohol in scales, m. p. 186° (Found: N, 6·8. $C_7H_8O_2NClS$ requires N, 6·8%).

(*b*) 3-Chlorotoluene-6-sulphinic acid, prepared from 5-chloro-*o*-toluidine (b. p. 245—247°/745 mm.) by the method already described, was isolated as a mass of radiating needles, m. p. 102—103°. The *barium* salt crystallised from dilute solution in long flat needles [Found: Ba, 23·1; H_2O, 11·9. $(C_7H_6O_2ClS)_2Ba,4H_2O$ requires Ba, 23·3; H_2O, 12·2%] or as dihydrate (Found: H_2O, 6·8%) in a hard mass of scales from concentrated solutions quickly cooled. By oxidation it furnished the 6-sulphonate which, as its chloride, m. p. 54°, and amide, m. p. 185°, showed, was identical with the product obtained from *m*-chlorotoluene by sulphonation (Wynne, *loc. cit.*), thus confirming the constitution of that acid regarded as probable by Schraube and Romig (*Ber.*, 1893, **26**, 578).

(II) *Dichlorotoluene-sulphinic and -sulphonic Acids.*—As Cohen and Dakin were unable to confirm the statement that 2 : 3-dichlorotoluene, differing from its isomerides, gives two sulphonic acids on sulphonation, an independent scrutiny of the reaction was made by Dr. (now Prof.) Kenner some years later, to whom our thanks are due for his report which is summarised as follows:

2 : 3-Dichlorotoluene (50 g.), prepared by each of the first two of the three methods employed by Wynne and Greeves (*loc. cit.*), was sulphonated by shaking with 10% oleum (100 g.) at 50°, more of the acid (50 g.) being added at the end of 1½ hours. On completion of the reaction in the course of 3 hours, the product was poured on to ice, a trifling amount of unchanged dichlorotoluene removed by distillation with steam, and the solution neutralised by baryta. Following exhaustive extraction of the barium sulphate sludge, the contents of the solution were fractionally crystallised, which brought about the separation of two salts differing sharply in solubility and appearance—the less soluble, granules and the more soluble, needles. The less soluble barium salt gave an anhydrous *potassium* salt crystallising in scales or needles according to conditions (Found : K, 14·0. $C_7H_5O_3Cl_2SK$ requires K, 14·0%), a chloride in radiate needles, m. p. 50°, and an amide, m. p. 228°; whereas the more soluble barium salt furnished an anhydrous potassium salt crystallising in long prisms (Found : K, 14·0%), a chloride in large prisms, m. p. 88°, and an amide in scales, m. p. 183°.

In the first sulphonation, 2·8 g. of unchanged dichlorotoluene were recovered and 51·6 g. of potassium salt obtained (calc., 73·6 g.) exclusive of residues and last fractions, the yield from the less soluble barium salt being 44·7 g. as against 6·9 g. from the other. With the second sulphonation, these figures were 47·4 and 4·6 respectively. Later, it was shown (*v. infra*) that the sulphonic group occupies the 6-position in the less but the 5-position in the more soluble barium salt, whence it follows that, on the average, the production of the former is eightfold that of the latter.

On hydrolysis in orthophosphoric acid suspension with superheated steam, 2 : 3-dichlorotoluene was recovered from each salt, and that collected from the 6-isomeride, when resulphonated, gave the two series of derivatives as at first.

(i) 2 : 3-*Dichlorotoluene*-6-*sulphinic acid*. For a supply of the 5 : 6-dichloroaceto-*o*-toluidide (D.R.-P. 217,896) we were indebted to the Badische Anilin- und Soda-Fabrik. It was a white crystalline powder, crystallising from aqueous alcohol in needles, m. p. 143°, and on hydrolysis with its own weight of 50% sulphuric acid at 90° gave the sulphate—sparingly soluble in water—from which the base, m. p. 33°, b. p. 288—290°/739 mm., was obtained.

Suspended in dilute sulphuric acid, the sulphate submitted to the Gattermann reaction gave a product in which the whole of the sulphinic acid was retained in the filter cake. This, extracted by cold 2*N*-caustic soda, precipitated from the concentrated solution by acidification, and crystallised from ether, had m. p. 133°, dissolved readily in alcohol or ligroin but only sparingly in water, benzene or chloroform and was unstable. The *barium* salt formed rosettes of flattened needles [Found : Ba, 20·8; H_2O, 11·1. $(C_7H_5O_2Cl_2S)_2Ba,4H_2O$ requires Ba, 20·9; H_2O, 11·0%]. On oxidation, it furnished the 6-sulphonate which, as its chloride, m. p. 51—52°, and amide, m. p. 228°, showed, was identical with the salt obtained from the major sulphonation product of 2 : 3-dichlorotoluene.

(ii) 2 : 3-*Dichlorotoluene*-5-*sulphonic acid*. Although 5 : 6-dichloro-*m*-toluidine (m. p. 88°; Wynne and Greeves, *loc. cit.*) would have served the purpose, the source of this acid was 3-chloro-*o*-toluidine-5-sulphonic acid (D.R.-P. 218370, 229525) for a supply of which we were again indebted to the Badische Anilin- und Soda-Fabrik. This *o*-toluidine derivative crystallised from water in colourless needles, and its *barium* salt in blunt needles [Found : Ba, 21·4; H_2O, 8·3. $(C_7H_7O_3NClS)_2Ba,3H_2O$ requires Ba, 21·7; H_2O, 8·5%]. When heated with 75% sulphuric acid at 160°, it gave 3-chloro-*o*-toluidine as an oil, the acetyl derivative of which had m. p. 163° (cf. D.R.-P. 218370).

By Sandmeyer's method it was converted into the 2 : 3-dichlorotoluene-5-sulphonic acid, a 97% yield being obtained, which by its chloride, m. p. 88°, and amide, m. p. 184—185°, was shown to be identical with the minor sulphonation product of 2 : 3-dichlorotoluene. The *barium* salt crystallised in silky needles [Found : Ba, 20·1; H_2O, 8·5. $(C_7H_5O_3Cl_2S)_2Ba,3H_2O$ requires Ba, 20·5; H_2O, 8·1%], and the *sodium* salt in needles (Found : Na, 8·3; H_2O, 3·5. $C_7H_5O_3Cl_2SNa,\frac{1}{2}H_2O$ requires Na, 8·6; H_2O, 3·3%).

2 : 3-*Dichloro*-p-*toluidine*. The 2 : 3-dichloro-*p*-toluidine required for the preparation of 2 : 3-dichlorotoluene-4-sulphonic acid was obtained by reducing the 4-nitro-derivative formed when 2 : 3-dichlorotoluene is nitrated. Preliminary experiments showed that Cohen and Dakin's method of shaking the dichloro-derivative with 80% nitric acid (*loc. cit.*) was ill adapted for preparation in bulk. Nitration in glacial acetic acid solution was also unsatisfactory, but the following procedure gave good results and, without modification, was adopted also in later nitrations.

To 2 : 3-dichlorotoluene (64 g.), partly dissolved by stirring in concentrated sulphuric acid (50 c.c.), was added gradually a cold mixture of nitric acid (*d* 1·42, 1 mol.) with sulphuric acid

(50 c.c.) at a temperature not exceeding 50°. When all had been added, stirring was continued at 50° for ½ hour and while the mixture cooled. The nitro-compound, obtained in pellets, was easily collected on asbestos, the filtrate on dilution giving less than 0·5 g. of a pasty oil which on reduction and acetylation gave an impure acetyl derivative, m. p. 150—160°, indicating the probable presence of the 6-nitro-isomeride in minute amount.

The crude product formed a hard butter-like mass, m. p. 47°, and clarifying at 50°. Crystallised from petrol or from alcohol–acetic acid, it had m. p. 50—51° and was highly soluble in the usual organic solvents, but, although a mixture, could not be purified by fractional distillation under reduced pressure (*ca.* 270°/40 mm.) or by crystallisation. On reduction with tin and hydrochloric acid it gave a dichlorotoluidine which was not completely crystalline: the solid constituent had m. p. 40° and its acetyl derivative, m. p. 131°, but the acetyl derivative from the liquid melted at a higher temperature. Thereupon the acid solution obtained by reducing 40 g. of dichloronitrotoluene was fractionally neutralised, the liberated base being removed by distillation with steam, giving

(a) when ⅘ of the necessary soda added	11 g. solid base
(b) when ⅛ more of the necessary soda added	15 g. pasty ,,
(c) when excess of soda added	2 g. oily ,,

The oil, removed from the pasty separation by spreading on porous earthenware, left an additional 11 g. of the solid base, m. p. 40°, b. p. 271—276°/40 mm., giving an acetyl derivative, m. p. 131°, and being therefore pure 2 : 3-dichloro-*p*-toluidine (Cohen and Dakin gave m. p. 40—42° and 128—129° respectively). Extracted from the porous earthenware by chloroform, the oil (4 g.) united with (c) and acetylated proved to be a mixture of the foregoing, m. p. 131°, with a smaller amount of a substance, m. p. 140°, which by a mixed m. p. test was identified as 2 : 3-dichloroaceto-*o*-toluidide. The proportion of the 6-amino-derivative in the reduction product was estimated to be about 10%.

(iii) 2 : 3-Dichlorotoluene-4-sulphinic acid, prepared from 2 : 3-dichloro-*p*-toluidine, had m. p. 142° and its *barium* salt crystallised from hot solution in scales changing to needles after some time in the cold [Found: Ba, 23·1; H_2O, 3·7. $(C_7H_5O_2Cl_2S)_2Ba,H_2O$ requires Ba, 22·8; H_2O, 3·0%].

Potassium 2 : 3-*dichlorotoluene*-4-*sulphonate*, obtained from the sulphinate by oxidation, crystallised in anhydrous nacreous scales (Found: K, 13·9. $C_7H_5O_3Cl_2SK$ requires K, 14·0%); the *chloride* separated from ligroin in prisms, m. p. 40—41°; and the *amide* from alcohol in scales, m. p. 237° (Found: N, 6·2. $C_7H_7O_2NCl_2S$ requires N, 5·8%).

(iv) 2 : 4-*Dichlorotoluene*-5-*sulphinic acid*. The source of the acid was 4 : 6-dichloro-*m*-toluidine, part of which was isolated from the dichlorination product of aceto-*m*-toluidide (p. 693), and the remainder more easily as sole product from 2 : 4-dichlorotoluene by nitration and reduction as described for the 2 : 3-derivative (above). Conversion into sulphinic acid followed the usual procedure: the product separated from ether in irregular groups, m. p. 132°. The *potassium* salt, less soluble than the barium salt, crystallised in scales (Found: K, 13·8; H_2O, 6·7. $C_7H_5O_2Cl_2SK,H_2O$ reqnires K, 13·9; H_2O, 6·4%). By oxidation it gave potassium 2 : 4-dichlorotoluene-5-sulphonate, containing apparently $2H_2O$ of which only one mol. was lost at 190° (Found: K, 12·2; H_2O, 6·3. $C_7H_5O_3Cl_2SK,2H_2O$ requires K, 12·4; H_2O, 5·7%), but otherwise—as its chloride, m. p. 72°, and amide, m. p. 176°, showed—identical with the sulphonation product from 2 : 4-dichlorotoluene (Wynne and Greeves, *loc. cit.*).

(v) 2 : 6-*Dichlorotoluene*-3-*sulphinic acid*. The 2 : 6-dichloro-*m*-toluidine required for the preparation of this acid was obtained by nitrating 2 : 6-dichlorotoluene, b. p. 199—200°/760 mm., under the conditions described for the 2 : 3-isomeride (above). The nitro-derivative crystallised from alcohol–ether had m. p. 50° (cf. Cohen and Dakin, *loc. cit.*) and on reduction gave solely the amine, m. p. 57°, b. p. 266—268°/760 mm., identical with the 2 : 6-dichloro-*m*-toluidine isolated from the dichlorination product of aceto-*m*-toluidide (p. 693).

Owing to the marked instability of the diazonium sulphite solution, leading to the formation of much red tarry material during the passage of sulphur dioxide, conversion of the base into sulphinic acid, even at − 10°, gave only a poor yield. The acid had m. p. *ca.* 105° and its *barium* salt crystallised in clusters of needles [Found: Ba, 20·8; H_2O, 10·4. $(C_7H_5O_2Cl_2S)_2Ba,4H_2O$ requires Ba, 20·9; H_2O, 11·0%]. By oxidation this gave the 3-sulphonate which, as its chloride, m. p. 59°, and amide, m. p. 203°, showed, was identical with the salt obtained from 2 : 6-dichlorotoluene by sulphonation.

(vi) 3 : 5-*Dichlorotoluene*-2-*sulphinic acid*. This was prepared from 3 : 5-dichloro-*o*-toluidine obtained by passing the calculated quantity of chlorine slowly into a cold solution of 5-chloroaceto-*o*-toluidide (100 g.) in glacial acetic acid (200 g.) and some hours later, after warming the

whole to 75° and adding water at 75° (175 c.c.), allowing it to cool. From the separation consisting of almost pure 3 : 5-dichloroaceto-*o*-toluidide (60 g.), m. p. 180°, the base, m. p. 45°, was isolated after hydrolysis by boiling with hydrochloric acid (5 pts.) during 8 hours. The sulphinic acid derived from it was the most stable of the isomerides and, recrystallised from ether or petrol, formed clusters of scales, m. p. 115—116°. Its *barium* salt crystallised in scales [Found : Ba, 20·3; H_2O, 11·9. $(C_7H_5O_2Cl_2S)_2Ba,4H_2O$ requires Ba, 20·9; H_2O, 11·0%]. By oxidation the 2-sulphonate was obtained, the chloride, m. p. 43°, and amide, m. p. 168°, from which were identical respectively with the corresponding derivatives from the sulphonation product of 3 : 5-dichlorotoluene.

(vii) 3 : 5-*Dichlorotoluene*-4-*sulphinic acid*. In the best method found for preparing 3 : 5-dichloro-*p*-toluidine, chlorine (24 g.) was passed during 2 hours into 3-chloroaceto-*p*-toluidide (46 g.) dissolved in glacial acetic acid (184 c.c.), the solution after the lapse of a few hours being warmed to 70°, diluted with warm water (200 c.c.) and then allowed to cool. Hydrolysis of the crystalline separation of 2 : 3-dichloroaceto-*p*-toluidide (25 g.), m. p. 198°, required several hours' boiling with hydrochloric acid (20 pts.) for its completion. The base, b. p. 249°/772 mm., gave by Gattermann's method the sulphinic acid, m. p. *ca.* 127°, the highly soluble potassium salt of which on oxidation furnished *potassium* 3 : 5-*dichlorotoluene*-4-*sulphonate*, this forming moderately soluble, irregular crystals (Found : K, 13·2; H_2O, 6·7. $C_7H_5O_3Cl_2SK,H_2O$ requires K, 13·2; H_2O, 6·1%), convertible into the chloride, prisms, m. p. 56°, and the *amide*, scales, m. p. 154—155° (Found : N, 5·9. $C_7H_7O_2NCl_2S$ requires N, 5·8%).

Part of this work was carried out by one of us (W. A. S.) while holding the Sheffield Town Trustees' Fellowship in 1914—1915, and for the opportunity of collaborating later he was indebted to the British Dyestuffs Corporation Ltd.

The University, Sheffield. [*Received, March* 19*th*, 1936.]

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158. *Studies in the Toluene Series. Part VI. Nitration of the* 4-*Chlorotoluene*-2- *and* -3-*sulphonic Acids,* 3-*Chlorotoluene*-6-*sulphonic Acid and their Sulphonyl Chlorides.*

By W. Palmer Wynne.

The investigation of the products obtained by the nitration of the *o*-, *m*- and *p*-chlorotoluenesulphonic acids owed its origin to an attempt to use sulphonation as a means of purifying dichlorotoluenes prior to the study of their physical properties. When it was found that hydrolysis of the purified sulphonates failed to give the desired result, as impurity was introduced owing to some decomposition at the temperature employed, attention was directed to a more detailed study of the dichlorotoluenesulphonic acids themselves. These acids it was found could have their constitution determined either through the chloronitrotoluenesulphonic acids by exchange of the nitro-group for chlorine or through the dichlorotoluidines by replacement of the amino-group by the sulphonic radical, but not through the chlorotoluenesulphonyl chlorides, as the attempt to substitute chlorine for the SO_2Cl complex, through the agency of phosphorus pentachloride, led to profound decomposition.

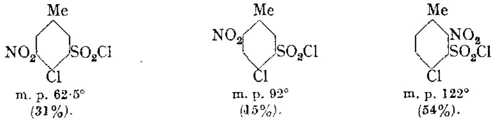
Nitration of the five readily accessible chlorotoluenesulphonic acids was undertaken in conjunction with Mr. A. Greeves (P., 1895, **11**, 152) and a large amount of material accumulated, but soon after its detailed examination had been begun the work was unavoidably interrupted and, although resumed at intervals with the aid of collaborators, has only now been brought to a stage suitable for publication.

Attempts to separate the nitration products from each of the five chlorotoluenesulphonic acids by fractional crystallisation of the barium, potassium or sodium salts from water or from alcohol were not successful, but from the derived sulphonyl chlorides isolation of the constituents of the mixture was, except in one case, achieved without undue difficulty. By interaction with alkali hydroxide, each chloride was converted into the alkali salt, the constitution of which was ascertained by reduction of the nitro- to the amino-group, exchange of the latter for chlorine, hydrolysis of the ensuing dichlorotoluenesulphonic acid and oxidation of the emergent dichlorotoluene to the corresponding dichlorobenzoic acid.

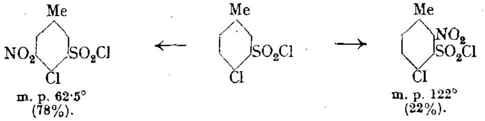
4-Chlorotoluene-3-sulphonic acid, the exception, with which this communication mainly deals differed from the other four in furnishing not merely all three rather than only two of the possible nitro-derivatives but also a mixture of sulphonyl chlorides resolvable apparently into four fractions, of which three were grouped round the m. p.'s 48—51°, 58—61° (main constituent 62·5°) and 120—122° (main constituent 122°) and the fourth over a wider range, 70—83° (main constitnent 92°). For a long time the relationship of the first two was a source of perplexity: they seemed to be the slightly impure forms of two isomerides melting at about 49° and 61°, yet m. p. determinations made with mixtures of equal weights of the two gave intermediate values such as 52—54° and a similar experience was encountered with the respective sulphonamides, which had the m. p.'s 184° and 196°, differed in solubility in dilute alcohol and in appearance as each separated from solution, but gave the mixed m. p. 191°.

Three years ago, the earlier conclusions—irreconcilable as they seemed to be among themselves and devoid of any quantitative significance—were discarded and the investigation begun anew. Eventually, by the use of petrol * in place of ligroin the separation m. p. 48—51°, which from other solvents had resisted fractionation, was shown conclusively to be a mixture of the isomerides of m. p. 62·5° and 122° in which the latter was present in remarkably small proportion, escaping recognition despite its sparing solubility until the final crystalline separations from the much concentrated mother-liquors were examined.

Reference to the table on p. 700 will show that the yield of crystalline sulphonyl chloride amounted at most to 64% of that calculated, the deficit being made up of non-crystalline chloride (7·3%)—presumably a mixture of isomerides—and of material not accounted for. Inasmuch as neither of the chlorides, m. p. 62·5° and 122°, was appreciably affected by being boiled for ½ hour with phosphorus pentachloride and oxychloride under reflux (as in the conversion of salt into chloride), the loss of material cannot be referred to decomposition involving the nitro-group. The composition of the crystalline prodnct, in so far as it can furnish a clue to that of the nitrated chlorotoluenesulphonate, indicates the preponderance of the fraction m. p. 120—122°, its yield being almost twice that of the fraction 47—60°, the next in order of abundance. Assigning to each fraction the constitution and m. p. of its chief constituent, the isomeric chlorides obtained from the products of nitration were:



In view of the element of uncertainty introduced by this loss in the conversion of salt into chloride, the nitration of 4-chlorotoluene-3-sulphonyl chloride was carried out under the conditions employed by Davies for *o*-chloro-derivatives (*J.*, **1921**, *119*, 853). The results as set out in the table on p. 704 showed that, whilst the yield was much more nearly quantitative, yet (i) the chloride, m. p. 92°, was not one of the products and (ii) the chloride, m. p. 122°, was now the minor product, being formed to a less extent than one-third of its isomeride:



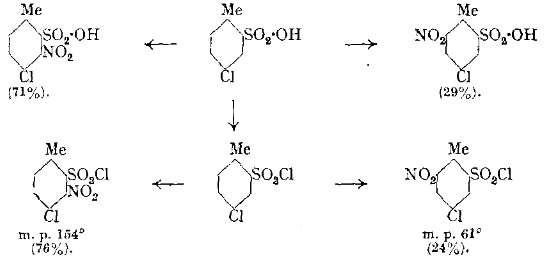
When it is remembered that the medium in which nitration took place was concentrated sulphuric acid in both cases, the agent fuming nitric acid, and the temperature range in

* The trivial names "petrol" and "ligroin" are used for the fractions of light petroleum, b. p. 40—60° and b. p. 60—80°, respectively.

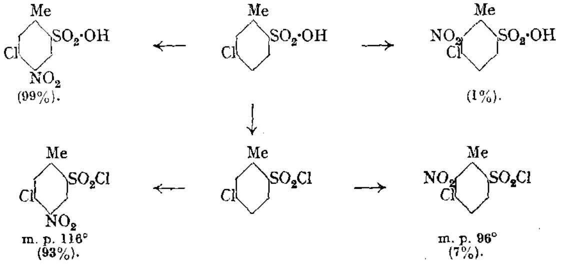
and duration of each operation practically the same, this difference in behaviour is sufficiently remarkable—search of the literature concerning the nitration of benzenesulphonic acid and its substitution products has failed to reveal a parallel case. The exchange of chlorine for hydroxyl within the sulphonic acid group does not at first sight appear to be a sufficient explanation of this difference of orientation unless, perhaps, the possibility of ionisation present in the one substance but absent in the other may be responsible. This question is discussed in detail in an addendum which follows these papers.

In addition to this 1 : 2 : 3 : 4-derivative, two others with the nitro-group intruded into the vacant 2- or 3-position were identified in the course of this investigation, being formed—each as the minor product of nitration whether acid or chloride be used—when :

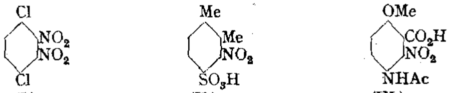
(i) either sodium 4-chlorotoluene-2-sulphonate or the 2-sulphonyl chloride is nitrated (pp. 704, 706)



(ii) either 3-chlorotoluene-6-sulphonic acid or the 6-sulphonyl chloride is nitrated (pp. 706, 707)



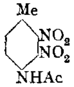
As the formation of nitro-derivatives of this type seems to occur only seldom, it may be of interest to record the following cases, in each of which all three isomerides were isolated,



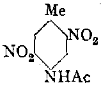
(I.) (II.) (III.)

the yield being intermediate between that of the other two in the case of (I) and (II) (for I, cf. Holleman, der Hollander, and van Haefter, *Rec. trav. chim.*, 1921, **40**, **323**; Macleod,

Pfund, and Kilpatrick, *J. Amer. Chem. Soc.*, 1922, **44**, 2268; Page and Heasman, J., 1923, **123**, 3247; for II, cf. Simonsen, J., 1913, **103**, 1144) but the smallest of the three in the case of (III) (Simonsen and Rau, J., 1917, **111**, 220). On the other hand, 2-nitro-4-acetamido-



m. p. 74°.



m. p. 122°.

toluene gives only two dinitro-derivatives and of these the 1 : 2 : 3 : 4-isomeride is the major product (Scott and Robinson, J., 1922, **121**, 844; Page and Heasman, *loc. cit.*, p. 3235).

Experimental.

(I) *Nitration of Sodium 4-Chlorotoluene-3-sulphonate.*—The 4-aminotoluene-3-sulphonic acid used for the preparation of the 4-chloro-acid was prepared by stirring vigorously a mixture of *p*-toluidine (107 g.) and concentrated sulphuric acid (100 g.) heated in a dish on a sand-bath until the appearance of boiling died down, the material became almost dry and incipient charring occurred. After being rendered alkaline, the product was freed from *p*-toluidine (7—12 g.) by blowing steam through the solution. Tested for the presence of the 2-isomeride (cf. Buff, *Ber.*, 1870, **3**, 796; Schneider, *Amer. Chem. J.*, 1886, **8**, 274) without result, the amino-acid was further shown to be uniform by the systematic examination of the derived chlorotoluenesulphonic acid and of the derivatives obtained by nitration of this chloro-acid.

To the sodium salt (115 g.) of the chloro-acid dissolved in four times its weight of sulphuric acid, a mixture of fuming nitric acid (*d* 1·52; 38 g.) with an equal weight of sulphuric acid was added gradually, with continuous stirring during 1·5 hours, the temperature, kept at 5—10° during the addition, being then allowed to rise to that of the laboratory. Baryta was used to remove the excess of sulphuric acid as being more convenient than lime; the filtrate, after removal of excess of baryta by means of carbon dioxide, contained both barium and sodium salts of the nitro-acid; the proportion of barium salt, calculated from the weight of carbonate precipitated by the addition of sodium carbonate solution, amounted to 30% on the average. After this exchange of barium for sodium the yield of anhydrous sodium salt (130 g.) was 94% of that calculated.

Fractional crystallisation of this product from water proved to be fruitless owing to the great solubility. From alcohol, in which the solubility at the boiling point was about 1 in 30, mixed separations were obtained, consisting of small hemispherical granules, attached limpet-like to the wall of the beaker, with small spherical clusters of microscopic prisms, often looking like drops of oil in suspension, or with soft, fine, flexible needles which became opaque when dry. The less soluble fractions were pale yellow; those more soluble were, like the final mother-liquors, dark reddish-brown. These crystalline forms, even when isolated, were not characteristic, recrystallisation invariably giving rise to mixed separations during the cooling of the solution: moreover, determinations of water of crystallisation in forms apparently similar were frequently not concordant. That failure to achieve a separation was not due to choice of salt became evident when the nitration product from the potassium salt proved equally troublesome. In the end, the isomeric chloronitrosulphonates were obtained by conversion of the nitrated salt into sulphonyl chloride, isolation of the isomeric chlorides by fractional crystallisation and hydrolysis of these by the appropriate alkali.

Conversion of the nitration product into sulphonyl chloride. After a preliminary separation into four fractions, the finely powdered, dry sodium salt (1 pt.) suspended in 30 g. quantities or less in phosphorus oxychloride (2·5 pts.) was boiled gently with phosphorus pentachloride (1 pt.) under reflux during ½ hour, the greater part of the oxychloride being then removed by distillation and the product stirred into water. Under these conditions the conversion was almost complete; the unchanged salt recovered in the final preparation amounted only to 8·6 g. from the 130 g. employed. This in its turn was submitted to the same treatment, and the resulting chloride worked up with the main bulk.

The chloride from the less soluble fractions of the sodium salt solidified under water; that from the later fractions was vaselin-like. These dissolved easily and completely in benzene. To the hot benzene solution of each preparation several times its volume of ligroin was added to free it from any soluble mineral salt retained by the moist chloride, the clear solution left to

crystallise, the mother-liquor distilled to remove the whole of the solvent, and the residual chloride fractionally crystallised from ligroin or, in the last stages, petrol. But only part of the dissolved chloride could be obtained crystalline: the remainder after removal of the solvent formed a viscid non-crystallisable residue: this in alcoholic solution was hydrolysed by sodium ethoxide with the separation of sodium chloride. By successive concentration of the alcoholic solution fractions wholly soluble in water were obtained, each of which after conversion into chloride furnished a crystalline separation and a non-crystallisable viscid residue. The table—from which it will be seen that four operations were necessary before the whole of the crystalline chloride obtainable from 130 g. of sodium chloronitrotoluenesulphonate (SO_2Cl calc., 128·2 g.) could be isolated—gives the initial fractionation, expressed in grams, of the product from the last of the series of nitrations.

Salt converted.	M. p. 47—60°.	M. p. 62—83°.	M. p. 112—120°.	Viscid chloride.
130·0	11·1	7·6	39·5	50·8 (49·4) *
49·4	5·5	5·0	3·8	29·6 (27·6)
27·6	5·8	0·1	0·4	17·2 (14·6)
14·6	*2·9*	—	*0·4*	*9·4 (7·3)* †
	25·3	12·7	44·1	7·3

* The weight of dry sodium salt obtained by hydrolysis with sodium ethoxide is given in parentheses.

† After hydrolysis, separation of the salt into a less and a more soluble fraction, followed by conversion of each into chloride, served only to regenerate the viscid product.

This yield of 82·1 g. or 64% of that calculated was the highest obtained. The isolation of the three isomerides, m. p. 62·5°, 92° and 122°, from these fractions led in the case of the first to the loss of much material and was rendered difficult owing to their ready solubility in the ordinary organic solvents other than light petroleum—eventually good results followed the use of petrol for the first (solubility about 2 g. in 100 c.c. at b. p.), ligroin with or without previous solution in a minimum amount of benzene for the second and benzene for the third.

Fraction, m. p. 48—60°. Repeated crystallisation of this material with petrol as solvent led to the accumulation of two fractions, one with m. p. 58—61°, the other and at first the larger with m. p. 48—52°—those of intermediate m. p. being resolvable gradually into these. From the former, the chloride, m. p. 62·5°, was isolated without much difficulty, but, with the latter, only after the most tedious fractionation was proof forthcoming that it was not the third isomeride (identification of this as the chloride, m. p. 92°, came later) but a mixture of the substance, m. p. 62·5°, with 4—5% of that melting at 122°.

With all fractions of low m. p., the solution in warm petrol became opalescent on cooling and a layer of " oil "—superfused mixture of the two chlorides—collected at the bottom of the beaker. Poured off, when it had become clear, and left over-night, the solution gave in addition to the crop of crystals a ring of " oil " above but in contact with its surface. This phenomenon became less marked with elimination of impurity, fractions of m. p. 59—62° being free from it.

Undisturbed, the layer of " oil " not infrequently remained for a day or two without crystallising: then, if in a thin layer, it would solidify in " diamond "-shaped forms, m. p. 47—49°. Despite the uniform appearance, these, dissolved in petrol, gave by slow spontaneous evaporation, crystals of mixed type, m. p. 49—53° or thereabouts, the final separations containing small rod-like prisms of the isomeride, m. p. 122°, which could be separated by hand. Thus 7·5 g. of this " oil," extracted by five successive 80 c.c. of petrol, gave the following fractions: m. p. 47—50°, 2·5 g.; m. p. 50—55°, 1·1 g.; m. p. 55—57°, 2·1 g.; m. p. 109—116°, 0·3 g. with a loss of 1·5 g. or 20%.

The slowness with which the separation of the constituents of the fraction, m. p. 48—60°, was achieved contrasts unfavourably with the more rapid parting of the isomerides from a mixture made by fusing together 4 g., m. p. 62·5°, and 1 g., m. p. 122°, at 140° for a short time. This solidified completely over-night, had m. p. 50—52°, and in one fractionation, involving nine successive crops of crystals, gave 3·3 g., m. p. 52—55°; 0·9 g., m. p. 58—61°; and 0·5 g., m. p. 109—119°—a total of 4·7 g.

The loss of material—the failure to obtain approximately as much crystalline substance from solution as taken up by it—seemed to be due for the most part to the final residues from crystallisation being oils, the constituents of which could not be separated by any method tried—freezing, fractional solution or hydrolysis. Accompanying the dissolution of fractions in the earlier stages of purification was a small amount of a viscid brown residue, less than 1% of the whole, which dissolved in water and was acid to test-paper, thus showing that slight hydrolysis had occurred between one crystallisation and the next. Such hydrolysis is not infrequent among

chlorides when kept over long periods (cf. Turner and Wynne, following paper); that it should be so soon detected with the chlorides of relatively low m. p. under investigation seemed remarkable—the more so, because the pure isomeride, m. p. 62·5°, does not show it even after the lapse of some months.

4-*Chloro*-5-*nitrotoluene*-3-*sulphonic acid*. The *barium* salt, obtained by hydrolysis of the sulphonyl chloride, m. p. 62·5°, crystallised in very pale yellow scales, becoming anhydrous when kept during 2 days in a desiccator over sulphuric acid [Found : Ba, 19·8; H_2O, 4·8. $(C_7H_5O_5NClS)_2Ba,2H_2O$ requires Ba, 20·4; H_2O, 5·3%]. The easily soluble potassium salt (+ H_2O), large, colourless, thin plates, and sodium salt (+ H_2O), small scales or felted needles, sometimes as dihydrate in felted needles, were also prepared. At 15°, the weight of anhydrous salt contained in 100 g. of aqueous solution was Ba 0·79 g., K 2·52 g., and Na 14·25 g.

The *chloride* had m. p. 62·5° (Found : Cl, 26·6. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). Professor G. M. Bennett has been good enough to measure the crystals of this chloride and reports as follows :

" The snbstance crystallises well from benzene or a mixture of this solvent with light petroleum, the crystals being anorthic with axial ratios $a : b : c = 1·385 : 1 : 1·159$; $\alpha = 99° 15'$, $\beta = 103° 51'$, $\gamma = 100° 15'$ and Federov angular elements : $d = 36° 47'$, $e = 80° 45'$, $ab = 76° 57'$, $f = 42° 3'$, $g = 76° 9'$. The following is a list of the forms observed and the mean values of the angles from three crystals measured on a two-circle goniometer :

	a(100).	*b*(010).	*c*(001).	*q*(011).	*p*(1̄11).	*R*(1̄01).	*Q*(01̄1).
φ	0° 0′	*76° 57′	29° 14′	*67° 8′	102° 45′	*164° 43′	270° 26′
ρ	90° 0′	90° 0′	18° 26′	*55° 26′	55° 7′	*31° 37′	45° 38′

" Barker classification angles: *cr* 33° 14′, *ra* 40° 45′, *am* 45° 25′, *mb* 31° 32′, *bq* 35° 46′, *qc* 42° 35′.

Fig. 1.

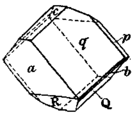


Fig. 2.

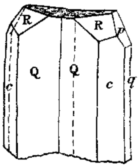


Fig. 3.

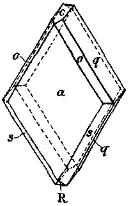
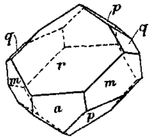


Fig. 4.



" The habit is shown in Fig. 1, but single crystals are rare, most crops consisting entirely of twinned crystals of the habit represented in Fig. 2. The twin plane is *q*(011). The mean angular values observed with seven of the twins were :

						on the second crystal.		
	q(011).	*c*(001).	*Q*(01̄1).	*R*(1̄01).	*p*(1̄11).	*Q*(01̄1).	*c*(001).	*q*(011).
φ	0° 0′	42° 35′	98° 32′	0° 0′	53° 45′	81° 28′	137° 25′	180° 0′
ρ	90° 0′	90° 0′	90° 0′	60° 43′	44° 33′	90° 0′	90° 0′	90° 0′

" Two faces often appear forming a re-entrant angle at the upper end of the twin, but these were so imperfect that they could not be exactly located or identified.

" The substance is biaxial, but the position of the optic axes was not found. The extinction on *Q* is at 35° to the edge *Qq*."

The *amide*, m. p. 196°, separated from dilute alcohol in long slender needles (Found : N, 11·5. $C_7H_7O_4N_2ClS$ requires N, 11·2%). It carbonised when its hydrolysis was attempted with either orthophosphoric or sulphuric acid and superheated steam.

4-*Chloro*-5-*aminotoluene*-3-*sulphonic acid*. Reduction of the nitro- to the amino-group was effected by adding " reduced " iron (12·5 g.) gradually to a boiling solution of the sodium nitro-salt (15 g.) in water (150 c.c.) acidified with concentrated sulphuric acid (12·5 c.c.). Usually much of the amino-acid separated before the addition was complete, the remainder being recovered from the filtrate. The *acid* (yield, 76% of that calculated) crystallised in clusters of very slender, colourless, silky needles, readily soluble in water but almost insoluble in alcohol (Found :

H_2O, 7·3. $C_7H_8O_3NClS,H_2O$ requires H_2O, 7·5%). The aqueous solution became violet on exposure to the air. The *barium* salt was highly soluble in water, but on the addition of alcohol crystallised in clusters of small, thin, almost colourless scales [Found: Ba, 22·4; H_2O, 4·2. $(C_7H_7O_3NClS)_2Ba,1\frac{1}{2}H_2O$ requires Ba, 22·7; H_2O, 4·5%]. The potassium salt (+ H_2O), scales from aqueous solution concentrated to a syrup but large, thin, colourless plates from dilute alcohol, and sodium salt (+ H_2O), thin, pale brown scales from dilute alcohol, were also prepared.

4 : 5-*Dichlorotoluene*-3-*sulphonic acid*. The *barium* salt, moderately soluble in water, crystallised in small, white, opaque, anhydrous granules, strung together in short rods [Found: Ba, 21·6. $(C_7H_5O_3Cl_2S)_2Ba$ requires Ba, 22·3%]. The potassium salt (+ H_2O), clear short needles which on exposure to the air became opaque, and sodium salt (+ H_2O), characteristic, thin, nacreons scales, both easily soluble in water, were also prepared. The *chloride*, m. p. 64°, readily soluble in petrol, crystallised from ligroin in rhomb-shaped monoclinic tables with an acute angle of 72° and an extinction angle of 18° (Found: Cl, 41·2. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide*, m. p. 158°, crystallised from alcohol in elongated, narrow, flat prisms (Found: N, 6·2. $C_7H_7O_2NCl_2S$ requires N, 6·1%).

Suspended in concentrated sulphuric acid (30 c.c.), the sodium salt (4·9 g.), hydrolysed by steam at 190—210°, gave 3 : 4-dichlorotoluene (1·4 g.), b. p. 198—200°/756 mm., identified by oxidation with dilute nitric acid (*d* 1·16) at 150° to 3 : 4-dichlorobenzoic acid, m. p. 206·5°.

Fraction, m. p. 62—83°. Isolation of the isomeride, m. p. 92°, from the fraction, m. p. 62—83°, although tedious, did not present any special difficulty. After experience gained with earlier preparations, 24 g. of the chloride collected from two nitrations were crystallised from ligroin and resolved eventually into the following fractions:

m. p. 48—57°	3·0 g.	m. p. 80—83°	14·9 g.
57—60°	0·6	116—122°	1·3
64—75°	1·0	not accounted for	2·2

By watching the crystallisation, the main constituent of this fraction, consisting of characteristic small, pale yellow, opaque clusters of minute prisms of m. p. above 77°, could often be removed in part before the remainder came out of solution mixed with aggregates of small transparent scales of lower m. p.: mixtures which in the last resort had to be separated by hand.

For the final purification, dissolution in the minimum volume of benzene, followed by the addition of 2—3 volumes of ligroin, gave the best result. With fractions of m. p. 90° and above, the crystalline form became that of clusters of small, pale yellow prisms no longer opaque but clear. The solubility of the chloride, m. p. 92°, in each of the three solvents—petrol, ligroin and benzene—was intermediate between that of the other isomerides.

4-*Chloro*-6-*nitrotoluene*-3-*sulphonic acid*. The *barium* salt, obtained by hydrolysis of the sulphonyl chloride, m. p. 92°, crystallised in moderately soluble, narrow, elongated scales, light yellow when dry but changing to a dirty grey on exposure to sunlight [Found: Ba, 19·6; H_2O, 5·7. $(C_7H_5O_5NClS)_2Ba,2H_2O$ requires Ba, 20·4; H_2O, 5·3%]. The potassium salt, long, slender, pale yellow, anhydrous needles, and sodium salt (+ H_2O), small, opaque, pale yellow aggregates, were also prepared. At 15°, the weight of anhydrous salt contained in 100 g. of aqueous solution was Ba 1·72 g., K 2·85 g., and Na 7·30 g. The *chloride*, m. p. 92°, highly soluble in benzene, separated from ligroin in radiating aggregates of prismatic crystals or minute rhomb-shaped crystals of acute angle 78° and with straight extinction, or, in the last stages of purification, in characteristic, small, semi-opaque aggregates of minute prisms, m. p. 86—89° (Found: Cl, 26·7. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 188°, crystallised from dilute alcohol in short slender needles (Found: N, 11·4. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

4-*Chloro*-6-*aminotoluene*-3-*sulphonic acid*. This acid (yield, 58% of that calculated), crystallised in lustrous, flat, anhydrous needles, moderately soluble in water. The *barium* salt formed thin laminated prisms, easily soluble in water [Found: Ba, 18·6; H_2O, 21·7. $(C_7H_7O_3NClS)_2Ba,9H_2O$ requires Ba, 18·5; H_2O, 21·9%]. The potassium salt (+ H_2O), long, flat, moderately soluble needles, clustered together, and sodium salt (+ $5H_2O$), thin, easily soluble, glistening scales, were also prepared.

4 : 6-*Dichlorotoluene*-3-*sulphonic acid*. The *barium* salt crystallised in readily soluble, long, slender, flat needles [Found: Ba, 21·0; H_2O, 5·1. $(C_7H_5O_3Cl_2S)_2Ba,2H_2O$ requires Ba, 21·0; H_2O, 5·5%]. The potassium salt, slender, flat, anhydrous needles or long, acicular, monohydrated needles, and sodium salt (+ $1\frac{1}{2}H_2O$), long slender needles, both easily soluble, were also prepared. The *chloride*, m. p. 72°, easily soluble in ligroin, crystallised in radiating needles with high double refraction and a straight extinction, and had the habit of climbing up the side of the beaker above the solvent, whether petrol or ligroin (Found: Cl, 40·7. $C_7H_5O_2Cl_3S$

requires Cl, 41·0%). The *amide*, m. p. 178°, crystallised from dilute alcohol in long slender needles (Found : N, 6·1. $C_7H_7O_2NCl_2S$ requires N, 6·1%).

On hydrolysis with orthophosphoric acid (*d* 1·75) and steam at 230—240°, the potassium salt (2·6 g.) yielded a dichlorotoluene (0·9 g.), b. p. 192—194°/756 mm., which on oxidation with nitric acid (*d* 1·16) at 150° gave 2 : 4-dichlorobenzoic acid, m. p. 161°.

Fraction, m. p. 112—120°. Isolation of the pure isomeride, m. p. 122°, from this fraction was easily achieved by first adding ligroin cautiously to the warm solution in benzene to precipitate impurity and then either concentrating the clarified liquid to crystallising point or throwing out the chloride by addition of ligroin in large amount.

4-Chloro-2-nitrotoluene-3-sulphonic acid. The *barium* salt, obtained from the sulphonyl chloride, m. p. 122°, by hydrolysis, was easily soluble in hot water, forming, on cooling, supersaturated solutions from which later it crystallised in thin, nacreous, colourless scales [Found : Ba, 17·3; H_2O, 18·3. $(C_7H_5O_5NClS)_2Ba,8H_2O$ requires Ba, 17·6; H_2O, 18·4%]. From alcohol, in which it was much less soluble than in water, it separated in scales (Found : loss, 14·4. Calc. for $6H_2O$, 14·5%). The potassium salt, thin, lustrous, anhydrous scales, and sodium salt (+ $3H_2O$), long, prismatic, pale yellow needles or, more usually, short slender needles which when washed with water on the pump formed a white felted mass, were also prepared. At 15°, the weight of anhydrous salt contained in 100 g. of aqueous solution was Ba 11·91 g., K 18·50 g., and Na 13·44 g. The *chloride*, m. p. 122°, crystallised from ligroin in flat, prismatic, faintly yellow needles or from light petroleum (b. p. 90—100°) in stout prisms or prismatic needles terminated by an oblique end at an angle of 52° and having an extinction angle of 23°. It was the least soluble of the three isomerides (Found: Cl, 26·1. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 177°, crystallised from aqueous alcohol in small flat prisms or in slender needles changing over-night in the solvent to the prismatic form (Found: N, 11·0. $C_7H_7O_4N_2ClS$ requires N, 11·2%). It did not furnish ammonia by prolonged boiling with alcoholic sodium hydroxide.

4-Chloro-2-nitrotoluene was obtained when the sodium salt (10 g.), mixed with concentrated sulphuric acid, was heated at 220° in a current of steam. The yield was slightly less when the amide was used instead of the salt. It was identified by its crystalline form, m. p. 38·5°, and by conversion into 4-chloro-*o*-toluidine, m. p. 22° (acetyl derivative, needles, m. p. 138°).

4-Chloro-2-aminotoluene-3-sulphonic acid. This acid (yield, 60% of that calculated) crystallised from water, in which it was only sparingly soluble, in slender, silky, colourless, anhydrous needles. The *barium* salt formed faintly brown, small, flat needles or lustrous scales which decomposed at 140° [Found : Ba, 22·9; H_2O, 1·3. $(C_7H_7O_3NClS)_2Ba,\frac{1}{2}H_2O$ requires Ba, 23·4; H_2O, 1·5%]. The potassium salt, easily soluble, soft, anhydrous scales, and sodium salt (+ $1\frac{1}{2}H_2O$), thin elongated scales or prisms which became anhydrous when kept for a week in a desiccator over sulphuric acid, were also prepared.

2 : *4-Dichlorotoluene-3-sulphonic acid.* The *barium* salt, obtained from the sulphonyl chloride by hydrolysis, crystallised in easily soluble, radiate groups of short stumpy needles [Found : Ba, 21·6; H_2O, 2·5. $(C_7H_5O_3Cl_2S)_2Ba,H_2O$ requires Ba, 21·6; H_2O, 2·8%]. The potassium salt, easily soluble, anhydrons, thin scales, and sodium salt (+ H_2O), minute scales highly soluble both in water and in alcohol, were also prepared. The *chloride*, very soluble in ligroin, was obtained as an oil which solidified in an ice-bath and had m. p. 19·5° (Found : Cl, 40·7. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide* crystallised from dilute alcohol in slender flat needles, m. p. 188° (Found : N, 6·4. $C_7H_7O_2NCl_2S$ requires N, 6·1%).

Suspended in orthophosphoric acid (*d* 1·75), both the sodium salt (20·5 g.) and the amide (16 g.), when hydrolysed by steam at 240°, gave a dichlorotoluene, b. p. 195—197°/756 mm. (the yields being 7·6 and 4·5 g. respectively), which on oxidation with dilute nitric acid (*d* 1·16) at 150° furnished 2 : 4-dichlorobenzoic acid, m. p. 161°.

(II) *Nitration of 4-Chlorotoluene-3-sulphonyl Chloride.*—Nitration of the sulphonyl chloride, m. p. 54°, was carried out under the conditions described by Davies (J., 1921, **119**, 853), the chloride (90 g.) in fine powder being dusted into a mixture of fuming nitric acid (*d* 1·52, 45 c.c.) and concentrated sulphuric acid (112·5 c.c.) continuously stirred and kept at 20—30°. At the end of an hour, the suspended solid had become a mass of liquid globules which eventually coalesced, stirring being maintained during a further 3 hours. Poured on to ice, the product solidified : it was ground, and washed repeatedly with water, cold at first and afterwards warm, until free from acid. The yield amounted to 98 g., but of this 4·7 g. were lost by accident—the remainder, 93·3 g., dissolved completely in benzene. For the separation of the isomeric chlorides, the methods already described were employed, the constituent of lower m. p. in the initial fractionation being collected in the fraction, m. p. 51—61°, with the exception of

one crop of crystals (8·1 g.) of m. p. 47—49°. Separations having m. p.'s in the neighbourhood of 50° gave solutions in petrol which on cooling became opalescent and during spontaneous evaporation formed rings of " oil " above the surface, but fractionation was much less troublesome and purification easier than with the product obtained from the nitrated salt.

Despite repeated and careful search, no trace of the isomeride, m. p. 92°, was discovered—none existed in the fraction, m. p. 53—58°, which a test showed to be largely composed of the isomeride, m. p. 62·5°. From the table, which gives the results obtained in the examination of the nitration product, it will be seen that the proportion of the two isomerides, m. p. 62·5° and

M. p.	53—62°	122°	"oil"	not accounted for	Total.
Grams	62·9	18·0	2·5	9·9	93·3

122°, differs remarkably from that found when the salt was nitrated and afterwards converted into chloride (p. 700).

(III) *Nitration of Sodium 4-Chlorotoluene-2-sulphonate.*—In the original experiments, the 4-nitrotoluene-2-sulphonic acid required as the source of the chloro-acid was prepared by sulphonating *p*-nitrotoluene (1 pt.) with 23% oleum (2·5 pts.) at 50°, the yield amounting to 94% of that calculated. For a repetition of the earlier work sodium *p*-nitrotoluene-2-sulphonate (chloride, m. p. 46°) obtained by purchase was used.

Nitration of sodium 4-chlorotoluene-2-sulphonate (58 g.) in concentrated sulphuric acid solution was carried out exactly as described for the 3-sulphonate (p. 699), and the product isolated as sodium salt (64·8 g.), the yield being 93% of that calculated. Fractional crystallisation of the product from water, in which it was easily soluble, or from alcohol, in which the solubility was markedly less, led to no satisfactory result, but a separation of the two constituents was achieved without difficulty by conversion of the salt into the sulphonyl chloride. On crystallisation of this product from benzene or from benzene–ligroin the less soluble chloride, m. p. 154°, could be removed completely before the isomeride made its appearance. The table shows the yield of the various products.

M. p.	54—59°	154°	" oil " not examined further	not accounted for	Total
Grams	39·6	10·7	6·3	8·2	64·8

No trace of a third isomeride was encountered.

4-Chloro-6-nitrotoluene-2-sulphonic acid. The *barium* salt, obtained from the sulphonyl chloride, m. p. 61°, by hydrolysis, crystallised in sparingly soluble, slender needles [Found: Ba, 18·7; H_2O, 10·0. $(C_7H_5O_5NClS)_2Ba,4H_2O$ requires Ba, 19·3; H_2O, 10·0%]. The *potassium* salt (+ $\frac{1}{2}H_2O$), very small, opaque, spherical aggregates of minute needles, and *sodium* salt (+ $1\frac{1}{2}H_2O$), small opaque granules, both readily soluble in water but only sparingly in alcohol, were also prepared. The *chloride*, m. p. 60°, was easily soluble in benzene. From petrol it separated in well-formed small prisms (Found: Cl, 26·2. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%).

Professor G. M. Bennett has been good enough to measure the crystals of this chloride and reports as follows:

" The substance crystallises in the monoclinic system with axial ratios $a:b:c = 2{\cdot}073:1:1{\cdot}536$ and $\beta = 104°52'$. The following is a list of forms observed and of the means of angular measurements obtained from three selected crystals with the two-circle goniometer:

	$a(100)$.	$c(001)$.	$R(\bar{1}01)$.	$o(111)$.	$q(011)$.	$s(\bar{2}11)$.
ϕ	0° 0′	*75° 8′	116° 48′	*44° 6′	74° 42′	142° 1′
ρ	90° 0′	90° 0′	90° 0′	*43° 6′	33° 57′	46° 27′

" Barker classification angles: *cr* 31° 2′, *ra* 44° 6′, *am* 26° 31′, *bq* 33° 58′.

" The crystals are developed with *a* large (Fig. 3).

" The optic axial plane lies in *b*. One optic axis is seen to emerge almost perpendicular to the face *a*. The double refraction is strong and positive."

The *amide*, m. p. 167°, crystallised from dilute alcohol in radiate, long, slender needles (Found: N, 11·3. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

4-Chloro-6-aminotoluene-2-sulphonic acid. This *acid* (yield, 67% of that calculated) crystallised in sparingly soluble, very slender needles (Found: H_2O, 5·1. $C_7H_8O_3NClS,H_2O$ requires

H_2O, 5·2%). The *barium* salt formed small, sparingly soluble, anhydrous scales [Found : Ba, 23·3. $(C_7H_7O_3NClS)_2Ba$ requires Ba, 23·7%]. The potassium salt (+ H_2O), clusters of scales, and sodium salt (+ H_2O), scales, both readily soluble, were also prepared.

4 : 6-*Dichlorotoluene-2-sulphonic acid*. The *barium* salt crystallised in very sparingly soluble, anhydrous, silvery scales [Found : Ba, 21·7. $(C_7H_5O_3Cl_2S)_2Ba$ requires Ba, 22·3%]. The potassium salt (+ H_2O), somewhat sparingly soluble, small, glistening prisms, and sodium salt (+ H_2O), moderately soluble, long, flat needles, were also prepared. The *chloride*, m. p. 54°, was highly soluble in benzene, ligroin or petrol and after removal of the solvent frequently remained liquid until nucleated. It crystallised in small monoclinic tablets with an oblique extinction (extinction angle about 40°) (Found : Cl, 40·8. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide*, m. p. 186°, crystallised from dilute alcohol in thin flat needles (Found : N, 6·0. $C_7H_7O_2NCl_2S$ requires N, 6·1%).

On hydrolysis at 230—240° with steam, the sodium salt (8 g.), suspended in concentrated sulphuric acid, gave a dichlorotoluene (1·9 g.), b. p. 195—196°/765 mm., which on oxidation with dilute nitric acid (*d* 1·16) at 150° furnished 2 : 4-dichlorobenzoic acid, m. p. 161—162°.

4-*Chloro-3-nitrotoluene-2-sulphonic acid*. The *barium* salt, obtained from the sulphonyl chloride, m. p. 154°, by hydrolysis, crystallised in radiating groups of moderately soluble, colourless, long, brittle needles which became opaque on exposure to the air [Found : Ba, 18·7; H_2O, 13·1. $(C_7H_5O_5NClS)_2Ba,5H_2O$ requires Ba, 18·9; H_2O, 12·4%]. The potassium salt, readily soluble, radiate groups of small, slender, anhydrous needles, and sodium salt (+ $4H_2O$), radiate groups of short slender needles from highly concentrated solution, were also prepared. The *chloride*, m. p. 154°, crystallised from benzene in lustrous monoclinic needles with an extinction angle of 20° and was less soluble than its isomeride either in this solvent or in ligroin or petrol (Found : Cl, 26·1. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 183°, crystallised from alcohol in sparingly soluble, short, slender, soft needles (Found : N, 11·2. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

4-*Chloro-3-aminotoluene-2-sulphonic acid*. This acid crystallised in anhydrous slender needles and was more soluble in water than its isomeride. The *barium* salt, sparingly soluble in water, crystallised in very small aggregates of minute, glistening, anhydrous prisms, looking like a fine white sand when dry [Found : Ba, 23·2. $(C_7H_7O_3NClS)_2Ba$ requires Ba, 23·7%]. The potassium salt (+ H_2O), moderately soluble, four-sided tablets, and sodium salt (+ H_2O), lustrous, thin, square scales more soluble than the potassium salt, were also prepared.

3 : 4-*Dichlorotoluene-2-sulphonic acid*. The *barium* salt came out from solution in moderately soluble, anhydrous, coralline forms [Found : Ba, 21·8. $(C_7H_5O_3Cl_2S)_2Ba$ reqnires Ba, 22·3%]. The potassium salt, lustrous, elongated, anhydrous scales, and sodium salt (+ H_2O), lancet-shaped small needles, both readily soluble, were also prepared. The *chloride*, m. p. 49°, highly soluble in benzene, crystallised in stout monoclinic prisms or from petrol in monoclinic needles with straight extinction (Found : Cl, 41·0. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide*, m. p. 186°, separated from dilute alcohol in long, soft, silky needles (Found : N, 6·4. $C_7H_7O_2NCl_2S$ requires N, 6·1%). Mixed with 4 : 6-dichlorotoluene-2-sulphonamide (m. p. 186°), it melted at 160°.

On hydrolysis, the sodium salt (6·8 g.), suspended in concentrated sulphuric acid at 230°, gave a dichlorotoluene (2·3 g.) consisting mainly of a fraction, b. p. 198—201°/765 mm. (1·5 g.), which on oxidation with dilute nitric acid (*d* 1·16) at 150° gave 3 : 4-dichlorobenzoic acid, m. p. 206°.

(IV) *Nitration of 4-Chlorotoluene-2-sulphonyl Chloride*.—Fused 4-chlorotoluene-2-sulphonyl chloride, m. p. 24° (80·5 g.), nitrated under the same conditions as the 3-isomeride (p. 703), furnished a product (92 g.) which was completely soluble in benzene. Concentrated to 155 c.c., the solution gave a separation in elongated prisms, m. p. 153—154° (13·2 g.), and by further concentration to 100 c.c. deposited smaller but similar prisms, m. p. 154° (2 g.). From the mother-liquor, diluted with three times its volume of petrol, a third crop of small prisms was obtained, m. p. 154° (2·5 g.), but after removal of these the solution, left over-night, furnished an entirely different crystallisation in large, yellow, prismatic forms, m. p. 61° (26·2 g.). Subsequent concentration of the 400 c.c. of solution to 45 c.c. (now mainly benzene), followed by addition of three times the volume of petrol, led to the separation of an oil (13 g.), which after removal deposited large prisms, m. p. 60° (6·2 g.), while the mother-liquor by spontaneous evaporation gave successive crops (12·5 and 7·2 g.) of similar crystals, m. p. 60°, and eventually from the accumulation of oil (14·8 g.) by drying on porous earthenware a final separation in prisms, m. p. 58—59° (3·9 g.). As was the case with the nitration product from the sulphonic acid, the nitrated chloride was resolved sharply and speedily into its constituents. No trace

of a third isomeride was detected. Summarised, the results obtained in the nitration were:

M. p.	61°	154°	"oil" not further examined	not accounted for	Total
Grams	56·0	17·7	10·9	7·4	92·0

these do not differ materially from those recorded for the nitration of the salt (p. 704).

(V) *Nitration of 3-Chlorotoluene-6-sulphonic Acid.*—As the 6-sulphonic acid is the only product formed when *m*-chlorotoluene is heated with three times its weight of pure (100%) sulphuric acid at 70° (Wynne, J., 1892, **61**, 1075; cf. Schraube and Romig, *Ber.*, 1893, **26**, 578), its nitration was effected by adding the requisite quantity (1·5 mols.) of nitric acid (*d* 1·48) gradually to the sulphonation melt at 0—5° and afterwards allowing the temperature gradually to become normal in the course of 2 hours. Converted into potassium salt and fractionally crystallised, the product from 200 g. of *m*-chlorotoluene amounted to 450 g. or 98% of that calculated. Of this, 446 g. were obtained in long, slender, anhydrous needles, but the last two separations, amounting only to 4 g. after recrystallisation, were in small anhydrous scales. Until nitration of 3-chlorotoluene-6-sulphonyl chloride under Davies's conditions had been shown to yield two isomerides in widely different proportion, this relatively minute fraction did not receive attention. But, on examination, it proved to be the potassium salt corresponding to the chloride, m. p. 96°, which forms the minor product from the alternative source (p. 707).

3-*Chloro*-4-*nitrotoluene*-6-*sulphonic acid.* The barium salt, obtained from the sulphonyl chloride, m. p. 116°, by hydrolysis, crystallised in sparingly soluble, long, pale orange needles [Found: Ba, 19·6; H_2O, 8·0. Calc. for $(C_7H_5O_5NClS)_2Ba,3H_2O$: Ba, 19·8; H_2O, 7·8%. Schraube and Romig found $2H_2O$]. The potassium salt, long, pale yellow, somewhat sparingly soluble, anhydrous needles, and sodium salt (+ H_2O), radiate groups of moderately soluble, pale yellow needles, were also prepared. The *chloride*, m. p. 116°, crystallised in pale yellow, lustrous prisms with a high double refraction and straight extinction and dissolved readily in benzene but only sparingly in ligroin (Found: Cl, 26·6. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). On digestion with boiling alcoholic potash both chlorine atoms were rapidly removed. The *amide*, m. p. 170°, crystallised from aqueous alcohol in thin long needles (Found: N, 11·1. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

3-*Chloro*-4-*aminotoluene*-6-*sulphonic acid.* The acid (yield, 76% of that calculated) crystallised in somewhat sparingly soluble, anhydrous, slender needles. The *barium* salt formed pale yellow, moderately soluble aggregates of minute needles [Found: Ba, 22·4; H_2O, 5·6. $(C_7H_7O_3NClS)_2Ba,2H_2O$ requires Ba, 22·4; H_2O, 5·9%]. The potassium salt, highly soluble aggregates of small anhydrous scales, and sodium salt (+ H_2O), very small scales from 92% alcohol, were also prepared.

The constitution assigned to the nitro-derivative by Schraube and Romig was confirmed by conversion of the amino-compound into dichlorotoluenesulphonyl chloride (m. p. 84°) and sulphonamide (m. p. 190°), respectively identical with the corresponding derivatives of the acid obtained from 3 : 4-dichlorotoluene by sulphonation (Wynne, J., 1892, **61**, 1062).

Professor G. M. Bennett has been good enough to measure the crystals of this chloride and reports as follows:

"This substance crystallises in the monoclinic system with axial angle β = 98° 15′ and axial ratios $a : b : c$ = 1·429 : 1 : 0·747. Barker classification angles: $a(100) : m(110)$ = 54° 44′, $c(001) : r(101)$ = 25° 37′, $r(101) : a(100)$ = 56° 8′, $b(010) : q(011)$ = 53° 31′. The following table gives a list of the forms observed and the mean angular measurements obtained with the two-circle goniometer from three selected crystals:

	a(100).	r(101).	m(110).	q(011).	p(111).
ρ	90° 0′	90° 0′	*35° 16′	*53° 31′	56° 10′
ϕ	0° 0′	56° 8′	0° 0′	*81° 45′	110° 57′

The habit of the crystals is compact with r(101) prominent (Fig. 4).

"The substance is doubly refracting and it was confirmed that the extinction divides the face r(101) symmetrically and perpendicular to the edge ra. The position of the optic axes could not be observed."

3-*Chloro*-2-*nitrotoluene*-6-*sulphonic acid.* The *barium* salt, obtained by hydrolysis of the sulphonyl chloride, m. p. 96°, crystallised in sparingly soluble, glistening, pale yellow, anhydrous scales [Found: Ba, 22·3. $(C_7H_5O_5NClS)_2Ba$ requires Ba, 22·5%]. The potassium salt, pale yellow, anhydrous scales, and sodium salt, radiate groups of pale yellow, slender, anhydrous

needles, both easily soluble, were also prepared. The *chloride*, m. p. 96°, crystallised from petrol in aggregates of small radiating plates with oblique extinction, opaque in the mass and more soluble than the 4-nitro-derivative (Found: Cl, 26·1. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 176°, separated from 25% alcohol in lustrous nacreous scales (Found: N, 11·0. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

3-*Chloro-2-aminotoluene-6-sulphonic acid*. The *acid* (yield, 52% of that calculated) crystallised in slender, sparingly soluble needles (Found: H_2O, 7·0. $C_7H_8O_3NClS,H_2O$ requires H_2O, 7·5%).

2 : 3-*Dichlorotoluene-6-sulphonic acid*. The *sodium* salt formed sparingly soluble, thin scales (Found: Na, 8·0; H_2O, 6·0. $C_7H_5O_3Cl_2SNa,H_2O$ requires Na, 8·2; H_2O, 6·4%). The chloride, m. p. 54°, did not depress the m. p. of 2 : 3-dichlorotoluene-6-sulphonyl chloride (Silvester and Wynne, this vol., p. 694) and its amide had m. p. 228°.

(VI) *Nitration of 3-Chlorotoluene-5-sulphonyl Chloride.*—For the preparation of the sulphonyl chloride, *m*-chlorotoluene (50 g.) was sulphonated in carbon disulphide solution with an equal weight (4 g. excess) of chlorosulphonic acid. After removal of the solvent and conversion of the product into sodium salt, a small amount (1·8 g.) of insoluble material was removed by filtration and proved to be 4 : 4′-*dichloro*-3 : 3′-*dimethyldiphenylsulphone*; this crystallised from benzene–petrol in small lustrous prisms, m. p. 130° (Found: Cl, 22·6. $C_{14}H_{12}O_2Cl_2S$ requires Cl, 22·5%).

For nitration, 3-chlorotoluene-6-sulphonyl chloride (56 g.) in fine powder was added gradually with continuous stirring to a mixture of nitric acid (*d* 1·5, 28 c.c.) and concentrated sulphuric acid (70 c.c.) at 25—30°, above which the temperature was not allowed to rise. At the end of 45 minutes, small solid globules began to separate and an hour later, when the operation was stopped, the mixture had become almost semi-solid. Washed free from acid and dried, the product (65·4 g.) dissolved completely in benzene, but the addition of several times the volume of ligroin precipitated the greater part (49 g.) of the main constituent, m. p. 116°. After removal of the solvent and extraction of the residue (16·4 g.) with successive quantities of petrol, followed by fractional separation from these solutions, an additional amount of this isomeride (4 g.) was isolated together with more soluble fractions (6·5 g.), m. p. 87—94°, from which by recrystallisation from this solvent uniform needles (4·1 g.), m. p. 96°, were eventually obtained. The later separations consisted of more soluble, ill-defined forms of much lower m. p. (3·7 g.) together with non-crystallisable oil (2 g.) and were not further examined.

The author desires to record his grateful acknowledgment of Professor Sir William Pope's kindness in placing a laboratory at his service which has made it possible for this investigation to be carried through. His thanks are due also to Miss E. Gertrude Turner for numerous analyses in the earlier stages of the work and to Mr. G. R. Purdy for the determinations of Cl and N, all of which were made by microchemical methods.

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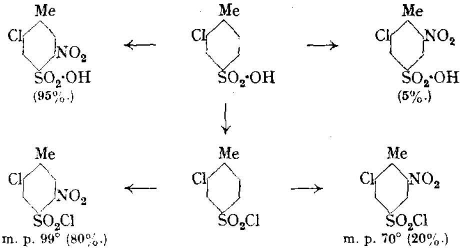
159. *Studies in the Toluene Series. Part VII. Nitration of 2-Chlorotoluene-4- and -5-sulphonic Acids and their Sulphonyl Chlorides.*

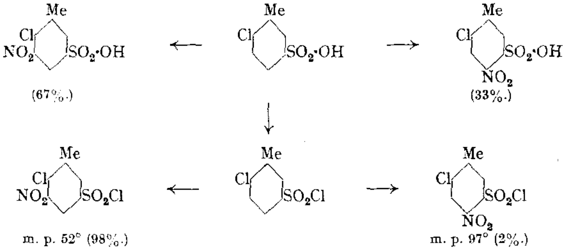
By (MISS) E. GERTRUDE TURNER and W. PALMER WYNNE.

NITRATION of the three *o*-chlorotoluenesulphonyl chlorides was investigated by Davies with the object of tracing the influence of the radicals present in the respective molecules on the orientation assumed by the NO_2-group, the constitution of the products being ascertained by means of the derived cresols (J., 1921, **119**, 853, 876; 1922, **121**, 785). Earlier, Wynne and Greeves had nitrated the potassium 2-chlorotoluene-4- and -5-sulphonates and arrived at the constitution of three of the products by the method already described (P., 1895, **11**, 152), but no attempt was then made to determine the relative proportion of the isomerides. The present communication removes that defect and moreover enables a comparison to be made between the yields obtained when in addition to the salt the derived sulphonyl chloride is nitrated under the closely similar conditions outlined in the preceding paper (p. 697). Expressed graphically, the following are the products isolated

(i) from the 4-derivatives:

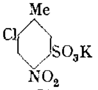


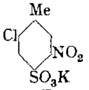
and (ii) from the 5-derivatives:

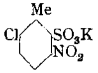


Unfortunately, a like comparison could not be made with the third isomeride, as potassium 2-chloro-5-nitrotoluene-6-sulphonate does not furnish a sulphonyl chloride but another type of product by interaction with phosphorus pentachloride in presence of oxychloride.

One remarkable feature of the interaction of pentachloride with the two sulphonates in which (a) the NO_2 and the SO_3K group are contiguous and (b) the NO_2 and the Cl group occupy relatively *para*-positions is the production of much reddish-brown non-crystallisable "oil" which does not furnish a definite salt when hydrolysed by aqueous caustic alkali or baryta. The isomeride (I), in which only one, the former, of these prerequisites is fulfilled,


(I.)


(II.)


(III.)

behaves normally, giving sulphonyl chloride with, it is true, an unusually large proportion of oil, but this is orange in colour and regenerates in part the sulphonate on hydrolysis. But (II), whilst giving sulphonyl chloride, gives also what seems to be a new type of reaction, the product of which at the moment of melting suddenly froths up the melting point tube: (III) also yields a similar compound as the sole crystalline product.

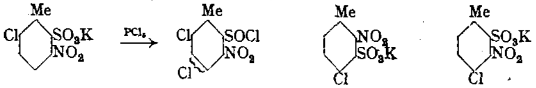
Analysed by Schoeller of Berlin, these compounds gave the following numbers:

From (II) C, 29·3; H, 1·5; N, 4·7; Cl, 36·9; S, 11·1; O (diff.), 16·4%.

From (III) C, 29·4; H, 1·5; N, 4·7; Cl, 36·5; S, 11·0; O (diff.), 16·9%.

$C_7H_4O_3NCl_3S$ requires C, 29·1; H, 1·4; N, 4·85; Cl, 36·9; S, 11·1; O, 16·65%.

We are indebted to Professor G. M. Bennett for the suggestion that these are sulphinyl chlorides in the production of which an additional chlorine atom has entered the ring. On



(IV.) (V.)

this view, not only has reduction of the SO_2Cl to the SOCl complex taken place, but simultaneously, to furnish the necessary chlorine, oxidation of one of the halogenated participants in the reaction must also have occurred.

It may be added that (I), in respect of its behaviour towards pentachloride, resembles the two *p*-chloro-derivatives (IV and V), from both of which, although the radicals NO_2 and SO_3K occupy contiguous positions, the products are sulphonyl chloride in good yield and pale brown oil from which sulphonate can be recovered by hydrolysis.

Experimental.

(I) *Nitration of Potassium 2-Chlorotoluene-4-sulphonate.*—In the original nitration experiments, *o*-toluidine-4-sulphonic acid, obtained as sole product by sulphonating *o*-toluidine hydrogen sulphate with twice its weight of 30% oleum at 20°, was the source of the potassium 2-chlorotoluene-4-sulphonate (Wynne and Greeves, P., 1895, **11**, 152). More conveniently the salt is prepared from the 2-chloro-derivative formed when toluene-4-sulphonyl chloride is chlorinated (cf. Davies, J., 1921, **119**, 860).

Nitrated in sulphuric acid solution under the conditions already described (this vol., p. 699), the dehydrated potassium salt (98 g.) gave a product which, after removal of the acid by baryta and of barium salt by potassium carbonate, separated from solution in the following fractions: from 1500 c.c., golden-yellow flat needles (72 g.); from the filtrate concentrated to 380 c.c., small golden-yellow prisms (21 g.); further to 50 c.c., similar prisms (11·3 g.); and to dryness, a residue (3·1 g.) largely inorganic. On recrystallisation the first separation seemed uniform and the second, so far as four-fifths, identical with it, but the third gave small crystalline granules. All were anhydrous.

Conversion of these fractions, suspended in phosphorus oxychloride, into sulphonyl chloride was incomplete unless the weight of phosphorus pentachloride used was twice that calculated. The product in each case was semi-solid and deep reddish-brown. Fractionally crystallised from ligroin, it was resolved into two isomerides together with much reddish-brown non-crystallisable oil from which nothing definite could be isolated either by prolonged standing or by hydrolysis with caustic alkali. The table shows the yields obtained:

	Wt. used.	Chloride, m. p. 91—95°.	Chloride, m. p. 69—70°.	Reddish-brown oil.
First separation ...	30 g.	14·8 g.	0·9 g.	9·1 g.
Second ,, ...	21	8·8	0·6	6·8
	51	23·6	1·5	15·9

From the third separation (11·3 g.) the product was mainly oil (5·7 g.), only a few needles (m. p. 65—66°) together with prisms (1·1 g., m. p. 90°) crystallising therefrom.

Although the amount of the isomeride of lower m. p. in each crystalline product is only about 6%, this proportion is probably too high. As will be seen later, the formation of the reddish-brown oil is associated exclusively with the conversion of (II) into sulphonyl chloride. If then, as seems not unreasonable, its weight be added to that of the chloride, m. p. 91—95°, the yield of the minor constituent will be reduced to 4% or thereabouts.

This fraction, m. p. 91—95°, proved to be a mixture. When first isolated, it did not as a rule fuse completely at this temperature—minute crystals remained, the pale yellow colour of the liquid then changed to reddish-brown and in the neighbourhood of 127° sudden decomposition occurred accompanied by much frothing. By repeated fractionation from light petroleum (b. p. 80—100°), 16·7 g. of this mixture gave 12·3 g. of sulphonyl chloride, m. p. 98—99°, which did not change colour below 150°, and 2·3 g. of a componnd which became brown at 95—100°, and had m. p. 128°, decomposing suddenly and almost simultaneously with much frothing.

That the production of this mixture is characteristic of the interaction of pentachloride with the 2-chloro-5-nitrotoluene-4-sulphonate, and does not depend on the presence of some un-

recognised third substance in the sulphonation melt, was shown by the use of sulphonate obtained by hydrolysis of (*a*) the sulphonyl chloride, m. p. 98—99°, isolated from the mixture, (*b*) the sulphonyl chloride, m. p. 98—99°, formed from 2-chlorotoluene-4-sulphonyl chloride by nitration (p. 711). In each case, the mixed product was reproduced—for example, in that of (*b*), the potassium salt (10 g.) with an equal weight of pentachloride gave prisms, m. p. 96—97° (3·2 g.), flat needles, decomp. at 124—125° (0·25 g.), and reddish-brown oil (2·2 g.), some unchanged salt (3·2 g.) being recovered.

Dichloro-5-nitrotoluene-4-sulphinyl chloride, $C_7H_4O_3NCl_3S$ (p. 708), separates from ligroin or light petroleum (b. p. 80—100°) in small, pale brown, monoclinic crystals which darken at 95—100° and decompose suddenly at 128°—if in quantity (0·05—0·1 g.) with an audible puff and the emission of much red nitrous gas. When boiled (*a*) with phosphorus oxychloride, a deep reddish-brown colour is developed; (*b*) with dilute nitric acid and silver nitrate, nitrous gas is evolved and silver chloride precipitated corresponding with 1 at. of chlorine (Cl found, 12·5; 1 at. Cl requires 12·3%); (*c*) with dilute (1%) caustic soda, rapid hydrolysis occurs giving a dark brown solution. Further it reduces nitric acid and ferric hydroxide—properties which, with its general instability and the evidence pointing to the continued presence of the NO_2 group, are in keeping with its suggested constitution. Warmed with dilute nitric acid, it is oxidised to a sulphonic acid, the crystalline *potassium* salt of which, dried at 120°, has the composition $C_7H_4O_5NCl_2SK$ (Found: K, 12·0. Required: K, 12·0% *).

2-*Chloro*-5-*nitrotoluene*-4-*sulphonic acid*. The *potassium* salt, sparingly soluble in water, crystallised in prismatic, pale yellow, anhydrous needles (Found: K, 13·1. $C_7H_5O_5NClSK$ requires K, 13·5%). The barium and sodium salts, chloride (m. p. 99°) and amide (m. p. 182°) had the properties described by Davies (*loc. cit.*, p. 865).

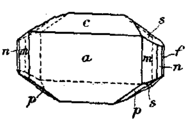
For measuring the crystals of the chloride we are indebted to Professor G. M. Bennett, who reports as follows :—

" This substance crystallises in the monoclinic system with axial angle β = 112° 48′ and axial ratios $a : b : c$ = 0·749 : 1 : 0·670. Barker classification angles: a(100) : m(110) = 34° 38′, c(001) : r(101) = 31° 34′, r(101) : a(100) = 35° 38′, b(010) : q(011) = 58° 17′. The following is a list of the forms observed and the mean angular measurements obtained with the two-circle goniometer from three selected crystals:

	a(100).	c(001).	m(110).	n(120).	b(010).	$s(\bar{1}21)$.	$p(\bar{1}11)$.
ρ	90° 0′	90° 0′	*55° 22′	35° 54′	0° 0′	56° 15′	*59° 37
ϕ	0° 0′	*67° 12′	0° 0′	0° 0′	all values	94° 1′	*119° 1

" The common habit of the crystals is, as shown in the figure, elongated along the b axis with a and c large.

" The snbstance has strong positive double refraction. The optic axial plane is parallel to b(010) and the acute bisectrix is perpendicular to a(100). There is strong inclined dispersion of the median lines."



2-*Chloro*-5-*aminotoluene*-4-*sulphonic acid*. The amino-acid, obtained in 77% yield, crystallised from water in very sparingly soluble clusters of short, stumpy, anhydrous needles. Coupled with β-naphthol, it furnished red lakes (cf. Meister, Lucius, and Brüning D.R.-P. 145908). The *barium* salt formed very sparingly soluble four-sided scales which became " electrical " when moved by spatula [Found: Ba, 23·0; H_2O, 2·8. $(C_7H_7O_3NClS)_2Ba,H_2O$ requires Ba, 23·0; H_2O, 3·0%]. The potassium salt ($2H_2O$) crystallised from supersaturated solutions on nucleation in ver slender needles.

2 : 5-*Dichlorotoluene*-4-*sulphonic acid*. The constitution assigned by Wynne and Greeve (*loc. cit.*) to the nitro-compound depended on conversion of the amino-acid into the dichlor acid, identified by comparison of the derived chloride (m. p. 43°) and amide (m. p. 196°) with the corresponding compounds obtained from authentic 2 : 5-dichlorotoluenesulphonic acid (Wynne J., 1892, **61**, 1052).

2-*Chloro*-6-*nitrotoluene*-4-*sulphonic acid*. 2-Chloro-6-nitrotoluene-4-sulphonyl chloride, m. p. 70° (cf. Davies, *loc. cit.*), crystallised from ligroin in flat elongated prisms with an oblique termination and an extinction angle of 42°. The barium and sodium salts and the amide (m. p. 182°) had the properties described by Davies (*loc. cit.*). The *potassium* salt formed moderately soluble, pale yellow, anhydrous, prismatic needles (Found: K, 13·2. $C_7H_5O_5NClSK$ requires K, 13·5%).

* Microanalysis made by Weiler of Oxford.

2-*Chloro*-6-*aminotoluene*-4-*sulphonic acid.* The amino-acid, obtained in 70% yield, was moderately soluble in boiling water, from which it separated in anhydrous glistening scales or small prisms. The *potassium* salt formed thin, small, anhydrous scales (Found: K, 14·8. $C_7H_7O_3NClSK$ requires K, 15·1%).

2 : 6-*Dichlorotoluene*-4-*sulphonic acid.* Obtained from the amino-acid in the usual way, the *potassium* salt crystallised from water in anhydrous, moderately soluble, "electrical" scales (Found: K, 14·0. $C_7H_5O_3Cl_2SK$ requires K, 14·0%). The chloride, m. p. 69°, crystallising from ligroin in massive anorthic crystals with extinction angles of 8° and 17° on adjacent faces, and the amide, m. p. 192°, were identified as derivatives of 2 : 6-dichlorotoluene-4-sulphonic acid (cf. Davies, *loc. cit.*, p. 872).

(II) *Nitration of* 2-*Chlorotoluene*-4-*sulphonyl Chloride.*—To obtain an additional supply of the 2-chloro-6-nitro-derivative, 2-chlorotoluene-4-sulphonyl chloride (75 g.) was nitrated under Davies' conditions and the dry product (87·5 g.), which dissolved completely in benzene, was fractionated first from ligroin and, after removal of most of the less soluble constituent (51·2 g. in prisms, m. p. 98—99°), later from petrol, whereby prisms (5·4 g.), needles, m. p. 69—70° (9·6 g.), and non-crystallisable oil (15·7 g.) were separated, leaving 5·6 g. not accounted for. The percentage of needles isolated, therefore, was substantially the same as that recorded by Davies, being 14·5 as against 13.

Of the 15·7 g. of oil, 6·2 g. had been absorbed by porous earthenware or filter-paper. The remainder, 9·5 g., after hydrolysis gave dry potassium salt (9·8 g.) from which by extraction with boiling 70% alcohol a separation (3·6 g.) in minute prisms was obtained, identified as the 2-chloro-6-nitro-salt by conversion into the 2 : 6-dichlorotoluenesulphonyl chloride (0·6 g.), m. p. 66—67°, and amide, m. p. 190°. On the assumption that this fraction was uniform, the oil will have contained an additional 3·5 g. of the isomeride, m. p. 69—70°, bringing up the yield to 13·1 g. or 19%. The residue (6·2 g.) insoluble in 70% alcohol yielded, by similar conversion presumably into dichlorotoluenesulphonyl chloride (0·9 g.), a non-crystallisable oil.

In Davies' experiments, the yield of nitro-derivative, m. p. 50—80°, was 109 g. from 100 g. of chlorotoluenesulphonyl chloride and from it prisms (80 g.), m. p. 99·2°, and needles (12 g.), m. p. 70°, were isolated, leaving 17 g. not accounted for. Relying on the melting-point curve of the isomerides to give the proportion more accurately than fractional crystallisation, he estimated the percentage of the constituent, m. p. 70°, to be 25·5 (27·4 g.). Evidently the point had been overlooked that for this to be the case, the residue (17 g.) left after removal of the crystalline material would need to consist almost wholly (15·4 g.) of the needle form. Probably, the proportion differs little from 20%.

(III) *Interaction of Potassium* 2-*Chloro*-5-*nitrotoluene*-6-*sulphonate with Phosphorus Pentachloride.*—The fact that 2-chloro-5-nitrotoluene-6-sulphonyl chloride so closely resembles the 4-sulphonyl chloride in constitution made a study of the interaction of the derived potassium sulphonate with phosphorus pentachloride imperative. 2-Chlorotoluene-6-sulphonyl chloride (80 g.), m. p. 72°, was therefore nitrated under Davies' conditions (J., 1921, **119**, 882), and the viscous product, after being washed free from acid, converted into barium salt, which by extraction with absolute alcohol gave the more soluble 6-sulphonate (43·6 g.) in approximately 50% yield. Interaction of the corresponding potassium salt, suspended in phosphorus oxychloride, with pentachloride led to the complete suppression of sulphonyl chloride, the only crystalline product isolated being the presumed *dichloro*-5-*nitrotoluene*-6-*sulphinyl chloride*, $C_7H_4O_3NCl_3S$, which crystallised from ligroin or light petroleum in small, pale brown prisms probably monoclinic, fused at 119°, decomposed almost simultaneously, at 119—120°, and in all other respects closely resembled the 4-sulphinyl derivative in properties (p. 710).

2-*Chloro*-5-*nitrotoluene*-6-*sulphonic acid.* The *barium* salt, obtained as above, crystallised from absolute alcohol in minute anhydrous scales but from water in very soluble, small spheres [Found: Ba, 21·0; H_2O, 3·0. $(C_7H_5O_5NClS)_2Ba,H_2O$ requires Ba, 20·9; H_2O, 2·7%. Davies found $7H_2O$]. The sodium salt, equally soluble, separated from absolute alcohol in minute anhydrous scales.

Whether heated with phosphorus pentachloride (1·5 pts.) and oxychloride (3·5 pts.) under reflux for 10 minutes in one experiment or in an open dish in a second, the colourless suspension of the sodium salt quickly became reddish-brown. After removal of most of the oxychloride, the product was in each case an oil which showed no sign of crystallisation in the course of a week and was completely soluble in benzene. The solution, freed from tarry matter by the addition of ligroin, gave on concentration separations in thin plates and finally reddish-brown non-crystallisable oil. In the two operations, the yields were:

Salt used.	Plates.	Oil.	Tar.	Total.
5 g.	1·2	2·7	1·0	4·9
7 g.	1·3	3·5	1·5	6·3

The separation in plates (2·5 g.), twice crystallised from light petroleum (b. p. 80—100°), formed practically colourless, prismatic needles (1·9 g.) which fused at 119° and decomposed suddenly at 119—120°, frothing up the melting point tube.

As the expected sulphonyl chloride (m. p. 61°; Davies, *loc. cit.*) had not been isolated, the oil (6·3 g.) was hydrolysed in alcoholic solution by caustic soda, and the solution, after neutralisation, evaporated to dryness. From the dry residue, absolute alcohol extracted a fraction (1·7 g.) which did not crystallise from this solvent but separated from aqueous solution (2—3 c.c.) in microcrystalline form (0·25 g.). This dried on porous earthenware may have contained sodium chloronitrotoluenesulphonate (Found: Na, 10·1. Calc. for $C_7H_5O_5NClSNa$: Na, 8·4%) arising from the presence of sulphonyl chloride in small amount in the oil, but no way was found of verifying this conjecture.

2-Chloro-5-aminotoluene-6-sulphonic acid. The *acid*, obtained in 77% yield, crystallised in sparingly soluble, long, flat, pointed needles [Found: H_2O, 2·8. $C_7H_8O_3NClS,1/3H_2O$ requires H_2O, 2·6%]. The *sodium* salt formed easily soluble, thin, elongated, anhydrous scales (Found: Na, 9·3. $C_7H_7O_3NClSNa$ requires Na, 9·4%).

2 : 5-Dichlorotoluene-6-sulphonic acid. The *barium* salt crystallised in sparingly soluble, anhydrous, irregular prisms [Found: Ba, 21·9. $(C_7H_5O_3Cl_2S)_2Ba$ requires Ba, 22·3%]. The easily soluble potassium salt formed small anhydrous scales, and the sodium salt (H_2O), elongated scales. The *chloride*, m. p. 38°, showed marked superfusion on removal of solvent (petrol), but when nucleated or cooled in a mixture of ice and salt became a solid mass of thin scales (Found: Cl, 40·9. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide*, m. p. 180°, crystallised from 90% alcohol in clusters of slender needles (Found: N, 6·0. $C_7H_7O_2NCl_2S$ requires N, 5·8%).

Hydrolysed at 230° in concentrated sulphuric acid suspension by superheated steam, the sodium salt (4·8 g.) gave a dichlorotoluene (2·3 g.), b. p. 196—198°/756 mm., which on oxidation at 150° with dilute nitric acid (*d* 1·16) furnished 2 : 5-dichlorobenzoic acid, m. p. 153°, thus confirming the constitution assigned by Davies.

(IV) *Nitration of Potassium 2-Chlorotoluene-5-sulphonate.*—Potassium 2-chlorotoluene-5-sulphonate (123 g.), prepared from Nevile and Winther's *o*-toluidinesulphonic acid and nitrated under the conditions already described (Wynne, this vol., p. 699), gave a mixture of two potassium chloronitrosulphonates (130·2 g.), one of which was unusually sparingly soluble in water. Dissolved in 2100 c.c. of boiling water, this product furnished a separation (75·7 g.) in small granules: these, redissolved in the same volume, crystallised uniformly in anhydrous, pale yellow scales (58·0 g.). Later separations from the two mother-liquors, each concentrated initially to 350 c.c. and eventually to dryness, gave a series of easily soluble fractions (78 g.) crystallised in either small brown prisms or pale yellow scales, both anhydrous, which on recrystallisation did not separate invariably in the one form or the other and for closer investigation were converted into sulphonyl chloride.

Much unchanged salt remained when any of these fractions, suspended in phosphorus oxychloride, was heated under the usual conditions with an equal weight of phosphorus pentachloride: for complete conversion double this amount had to be used. But while the product from the less soluble salt, being almost free from oil, was easily dealt with, that from the more soluble proved troublesome owing to the slow—and doubtless incomplete—separation of crystalline material from the orange-coloured "oil" that accompanied it. Even so, the difference in the proportion of the isomeric sulphonyl chlorides isolated from the products of nitration of the sulphonate and of the sulphonyl chloride was not less marked than with the corresponding 4-derivatives.

2-Chloro-3-nitrotoluene-5-sulphonic acid. The salts of this acid were obtained by hydrolysis of the sulphonyl chloride, m. p. 52°, with the appropriate alkali hydroxide. The *barium* salt crystallised in moderately soluble, long, slender, silky needles [Found: Ba, 19·6; H_2O, 8·; $(C_7H_5O_5NClS)_2Ba,3\frac{1}{2}H_2O$ requires Ba, 19·6; H_2O, 9·1%]. The potassium and sodium salts were anhydrous, but differed widely in solubility, the former separating in sparingly soluble, lustrous scales, difficult to wet when once dry. The *chloride*, m. p. 52°, obtained in 90% yield by the use of twice the calculated amount of phosphorus pentachloride, crystallised from ligroin in characteristic clusters of monoclinic, pale yellow prisms, some with straight extinction and others with an extinction angle of 40° (Found: Cl, 26·2. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *ami*

m. p. 201°, crystallised from 92% alcohol in short slender needles (Found: N, 11·0. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

2-*Chloro-3-aminotoluene-5-sulphonic acid*. The acid, obtained in 77% yield by reduction of the nitro-salt, crystallised from water in long, thin, easily soluble, anhydrous needles. It diazotised only very slowly at the ordinary temperature but more readily at 35—40°. The *potassium* salt, highly soluble in water, separated from 25% alcohol in long, thin, anhydrous scales (Found: K, 14·7. $C_7H_7O_3NClSK$ requires K, 15·1%). The sodium salt also formed anhydrous scales from 25% alcohol.

The constitution of these products was ascertained by conversion of the chloroamino- into the dichlorotoluene-5-sulphonic acid, the chloride (m. p. 90°) and amide (m. p. 184°) of which, by mixed m. p.'s, proved to be identical with the corresponding derivatives of 2 : 3-dichlorotoluene-5-sulphonic acid (Silvester and Wynne, this vol., p. 694).

2-*Chloro-4-nitrotoluene-5-sulphonic acid*. As repeated fractionation of the more soluble nitro-salt failed to bring about uniformity in crystalline appearance or marked variation in solubility, the whole in 10—12 g. quantities was converted into sulphonyl chloride under reflux with phosphorus pentachloride (2 pts.) and oxychloride (2·5 pts.). From 67·7 g., the yield of crude, semi-solid brown product was 61·3 g., which by fractionation gave prisms, m. p. 97°, irregular in form (12·4 g.) and an oil (42·3 g.) from which nothing crystalline had separated after the lapse of two months.

The *barium* salt, obtained by hydrolysis of the sulphonyl chloride, crystallised in moderately soluble, pale brown needles [Found: Ba, 20·2; H_2O, 5·9. $(C_7H_5O_5NClS)_2Ba,2H_2O$ requires Ba, 20·4; H_2O, 5·4%]. The potassium salt, anhydrous, and sodium salt ($\frac{1}{2}H_2O$) formed easily soluble, pale yellow needles. The *chloride*, m. p. 97°, sparingly soluble in ligroin, crystallised in elongated prisms with an oblique termination, of high double refraction, and with an extinction angle of 40° (Found: Cl, 26·2. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 172°, separated from 92% alcohol in easily soluble, thin, flat needles (Found: N, 11·0. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

2-*Chloro-4-aminotoluene-5-sulphonic acid*. The amino-acid, obtained in 62·5% yield, crystallised in sparingly soluble, short, anhydrous needles, and when dry, was wetted by water with difficulty. It has also been prepared by sulphonating 2-chloro-*p*-toluidine and, coupled with β-naphthol, furnishes scarlet lakes (cf. Badische Anilin- und Soda-Fabrik, D.R.-P. 175378, 217370). The *sodium* salt formed sparingly soluble, long but thin, anhydrous scales (Found: Na, 9·2. $C_7H_7O_3NClSNa$ requires Na, 9·5%).

Hydrolysis of the uncrystallisable oil (42·3 g.) by alkali left a resin (8 g.) which was not further examined. From the filtrate by reduction, a 62% yield of amino-acid (15·9 g.) was obtained, the sodium salt from which was unlike that just described and about twice as soluble, but on the addition of one-half the calculated quantity of hydrochloric acid gave a precipitate (7·5 g.) identified as the 4-amino-acid. That left in solution (8·1 g.), converted into dichloro-derivative, furnished an oily sulphonyl chloride (7·7 g.) which in the course of 10 days deposited radiate groups of needles (2·4 g.), but neither from these nor from the remaining oil (4·7 g.) was any definite substance isolated.

2 : 4-*Dichlorotoluene-5-sulphonic acid*. The *sodium* salt crystallised in moderately soluble, long needles (Found: Na, 8·7; H_2O, 6·1. $C_7H_5O_3Cl_2SNa,H_2O$ requires Na, 8·8; H_2O, 6·4%). The chloride, m. p. 72°, and amide, m. p. 176°, were identical with those formed from 2 : 4-dichlorotoluenesulphonic acid (Wynne and Greeves, P., 1895, **11**, 151).

The composition of the product obtained from potassium 2-chlorotoluene-5-sulphonate (123 g.) by nitration was: less soluble K salt (3-nitro-), 58 g.; more soluble K salt (4-nitro-), 26·5 (12·4 + 14·1, calc. from 7·5 g. of amino-acid on the basis of 62·5% yield); oil (sulphonyl chloride) from more soluble salt, calc. as K salt, 22·2; total, 106·7.

(V) *Nitration of 2-Chlorotoluene-5-sulphonyl Chloride*.—According to Davies (J., 1922, **121**, 788), nitration of 2-chlorotoluene-5-sulphonyl chloride furnishes a 90% yield of the 3-nitro-derivative, together with " several small rhombohedral crystals, m. p. 85—88° " occurring in final mother-liquors but in amount insufficient for analysis or identification. In view of the presence of much 4-nitro-compound in the product from the potassium salt (*supra*), repetition of the nitration of the chloride under Davies' conditions was thought desirable.

From 88 g. of the sulphonyl chloride, 99·7 g. of the dry nitro-compound, wholly soluble in ligroin, were obtained. Fractionally crystallised, this product gave 71·7 g. of the 3-nitro-derivative, m. p. 52°, together with 28 g. of an oil which slowly deposited needle-like crystals (16·1 g.) becoming almost semi-solid. These crystals on fractionation from petrol gave 6·6 g. of the 3-nitro-derivative, m. p. 52°, and an oil (9·1 g.) from which three separations in four-sided

scales (1·05 g.), m. p. 97°, were subsequently removed and identified as the 4-nitro-compound. Later, this oil became semi-solid : dried on a porous tile, it lost 2·5 g., leaving a solid which, fractionally crystallised from petrol, gave 2·7 g. of the 3-nitro-derivative, m. p. 52°, followed by separation of the 4-isomeride in small tablets (1·15 g.), m. p. 84—89°—these recrystallised had m. p. 97°.

Left during some weeks, the oil (11·3 g.) separated from the 16·1 g. of crystals had deposited needles (2·5 g.), m. p. 48—50°. These removed, the residue on hydrolysis with caustic potash gave 6·2 g. (chloride equiv., 5·8 g.) of the characteristic non-wetting scales of the potassium 3-nitro-sulphonate, but nothing definite could be isolated from the mother-liquors.

Summarised, the yield of isomeric nitro-derivatives from 2-chlorotoluene-5-sulphonyl chloride was 89·3 g. of 3-nitrosulphonyl chloride (m. p. 52°) and 2·2 g. of 4-nitrosulphonyl chloride (m. p. 97°).

It may be of interest to record that crystallised 2-chlorotoluene-5-sulphonyl chloride (85 g.) prepared in 1895 and kept in a stoppered bottle in the dark had in the course of 40 years become largely hydrolysed. No pressure was observed and only a faint odour of hydrogen chloride noticed on opening the bottle, but on extraction by warm water from the unchanged chloride (19·2 g.) the highly acid solution obtained, neutralised by caustic potash, gave a dry residue (74 g.) of potassium salt containing some chloride. This agrees well with the amount (71·5 g.) calculated on the assumption that atmospheric moisture had diffused inwards and hydrogen chloride outwards owing to imperfect stoppering.

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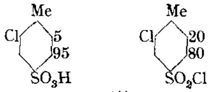
[*Received, March 19th, 1936.*]

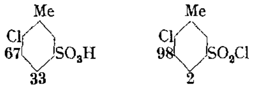
Addendum.

By G. Macdonald Bennett.

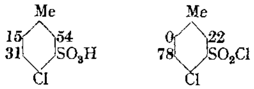
The experimental results recorded in the foregoing papers are collected in summarised form in the following formulæ, the figure attached to any position being the observed percentage of mononitration product in which the nitro-group has entered that position :



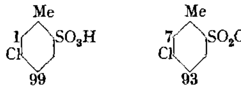
(A)



(B)



(C)



(D)

(E)

The most noticeable feature of these results is the difference in the proportions of th products when a sulphonyl chloride is subjected to nitration in place of the correspondin free sulphonic acid. Five isomeric acids have been studied (A—E), and each compare with the acid chloride on nitration. In three of these considerable nitration of the free aci takes place in the position *ortho* to the sulphonic group (A 95%, B 33%, C 54%), bu nitration of the corresponding chloride yields markedly lower proportions of *ortho*-sul stitution product (A 80%, B 2%, C 22%). In the remaining two instances there is n significant difference in behaviour between free acid and acid chloride, no *ortho*-nitratic

having been detected in one (D) and the variation in proportion of *ortho*-product in the other (E) being in the usual direction but almost negligible.

Substitution in the *ortho*-position is a common occurrence as a secondary feature of orientation by *meta*-directive groups such as NO_2,CHO,CO·R, CO_2H, etc., and this, occurring in spite of an inherent deactivating inductive effect, has been explained by Lapworth and Robinson as due to the association of a reagent such as nitric acid with the group in question, *ortho*-substitution being thereby favoured (*Mem. Manchester Phil. Soc.*, 1928, **72**, 43). The entry of the substituent into the position *ortho* to SO_3H is well known in nitrations (compare Obermiller, *J. pr. Chem.*, 1914, **89**, 70; 1930, **126**, 257) and, apart from contributory directive influences of other substituents already present (as in the cases now considered), this may in part be due to a similar cause as with the other *m*-directive groups above mentioned. The nitration of benzenesulphonic acid may, however, also be compared with the substitution of benzoic acid in alkaline solution recently re-examined by J. C. Smith (J., 1934, 213), who found the proportions: *o*- 47%, *m*- 33%, *p*- 20%. As regards benzenesulphonic acid the work of Limpricht (*Annalen*, 1875, **177**, 60) was corrected by Obermiller (*loc. cit.*), who found: *o*- 27%, *m*- 63%, *p*- 10%. The production of a considerable proportion of *para*-isomeride is the significant common feature of these two results which differentiates them in behaviour from such a substance as free benzoic acid. In both there appears to be a blend of *m*- with *op*-direction and an exaggeration of *o*-substitution. Bearing in mind that the benzoate in alkaline solution should be completely ionised and that the sulphonic acid, being a strong acid, should be completely ionised but, in solution in concentrated sulphuric acid, not completely dissociated, these two results are similar in type.

The important point here is that, whatever may be the mechanism responsible for these results, we must expect a suppression of both *o*- and *p*-products when the SO_3H group is converted into SO_2Cl, and this for several reasons. First, the SO_2Cl group will according to accepted views have a stronger electron-attracting inductive effect than SO_3H and so must tend to suppress *op*-substitution; secondly, the sulphonyl chloride is incapable of ionisation, so the group $SO_3^{\ominus}$ is eliminated; and lastly, if the *o*-nitration is in part due to an attraction of the nitric acid to the SO_2 group, the presence of the chlorine atom will counteract this by reducing any slight basic property of this group.

The operation of the change from acid to acid chloride upon orientation in nitration has already been noted in some analogous cases. Some figures for benzoic and benzylsulphonic acids are:

Substance nitrated.	Products, %. *m*-.	*o*-.	Reference.
$C_6H_5 \cdot CO_2H$ (at 0°)	80	18·5	Hollemann, *Rec. trav. chim.*, 1899, **18**, 267.
$C_6H_5 \cdot COCl$ (at − 12·5°)	90	8—10	Cooper and Ingold, J., 1927, 836.
$C_6H_5 \cdot CH_2 \cdot SO_3H$ (at − 5—10°)	14	33·5	Ingold, Ingold, and Shaw, J., 1927, 813.
$C_6H_5 \cdot CH_2 \cdot SO_2Cl$	51	17	,, ,, ,, ,,

However, the nitration of benzenesulphonyl chloride itself, which is the most directly relevant case, appears not to have been studied hitherto. A study of this is now being made in Sheffield and it has been found that nitration with mixed acid yields approximately 90% of the *m*-product. A full account of this work will be published in due course. This result in conjunction with that of Obermiller quoted above (*o*-direction by SO_3H, 27%) confirms the tendency under discussion.

Other features of the results require little comment. The familiar principles that *op*-directive influences tend to take precedence of so-called *m*-directive effects, and that the *o*/*p* ratio for the methyl group is high and that of the chlorine atom is low suffice to account in a general way for the observations in cases A, C, D and E. Thus chlorine dominates the substitution of A, its low *o*/*p* ratio leading to attack in position 5 rather than 3, and the high *o*-directing power of methyl causes position 6 to be the next favoured. The same high *o*-directive power of methyl is again evident with C. The SO_3H group here acts chiefly to suppress substitution *para* to itself, and SO_2Cl inhibits more efficiently in both *p*- and *o*-positions. In D, chlorine and methyl jointly direct into position 4 with 2 as secondary

position. Methyl and chlorine again show competitive *o*-direction in E, the SO_3H and the SO_2Cl group serving as restraints to prevent attack of position 3.

The substitution of B, although the effect of exchange of acid and acid chloride groups is clear, is nevertheless remarkable in that no reason is apparent why substitution does not occur to a considerable extent in position 6 between methyl and sulphonic acid groups.

THE UNIVERSITY, SHEFFIELD. [*Received, March 19th*, 1936.]

160. *X-Ray Crystallographic Measurements on Phrenosinic (Cerebronic) Acid and its Oxidation Product.*

By (MISS) D. M. CROWFOOT.

THE problem of the constitution of phrenosinic acid has recently been attacked by the methods of *X*-ray crystallography by Chibnall, Piper, and Williams (*Biochem. J.*, 1936, **30**, 105), whose results lead to the conclusion that this acid is a mixture of straight-chain α-hydroxy-acids, probably $C_{26}H_{52}O_3$, $C_{24}H_{48}O_3$, and even $C_{22}H_{44}O_3$, which accordingly on oxidation gives rise to a mixture of the *n*-fatty acids $C_{25}H_{50}O_2$, $C_{23}H_{46}O_2$, $C_{21}H_{42}O_2$. These conclusions agree with Levene and Taylor's experiments (*J. Biol. Chem.*, 1928, **80**, 227) in so far that the mean composition of the mixture of acids obtained on oxidation approximates closely to that of an acid $C_{24}H_{48}O_2$. On the other hand, the authors agree with Klenk and Diebold (*Z. physiol. Chem.*, 1933, **215**, 79) by confirming the presence in the oxidation product of acids containing an odd number of carbon atoms; they further suggest that the latter authors' method of fractionating their product may have led to the isolation of pure tricosanoic acid.

Through the kindness of Professor Robinson, it has been possible to examine both Klenk's preparation of cerebronic (phrenosinic) acid and the oxidation product, and to compare them with the synthetic acids $C_{24}H_{48}O_2$ and $C_{23}H_{46}O_2$ described by Ashton, Robinson, and Smith (this vol., p. 283). For better comparison, *X*-ray measurements were also made of the potassium salts of the last two acids and of the oxidation product. The main results obtained are in the table.

These measurements substantially confirm the conclusions reached by Chibnall, Piper, and Williams. The $d_{(001)}$ values here recorded for Klenk's preparation of the oxidation product are definitely lower than those found by the above authors (57·1, 52·0, for the lowest fractions), *i.e.*, are nearer to those of pure tricosanoic acid. Indeed, the *C*-polymorphic form of the oxidation product gives a *c* spacing almost identical with that attributed in the literature by extrapolation to tricosanoic acid itself (Francis, Piper, and Malkin, *Proc. Roy. Soc.*, 1930, **128**, 214).

It is, however, quite certain from the observations here recorded that Klenk's specimen is not pure tricosanoic acid, in spite of the process of purification to which it has been submitted. Pure tricosanoic acid proves not to crystallise in the normal *B*-form, and also cannot be maintained in the *C*-modification down to room temperature. Moreover, the molecular weight of Klenk's acid found by the *X*-ray method is higher than that required for pure $C_{23}H_{46}O_2$, being nearer to that for $C_{24}H_{48}O_2$, and the *c* spacing of its potassium salt is decidedly longer than that of pure tricosanoic acid. Taken together, the measurements indicate that Klenk's oxidation product is mainly tricosanoic acid, and that it is contaminated with an acid or acids of longer chain length, probably $C_{25}H_{50}O_2$ among others, as suggested by Chibnall, Piper, and Williams. Comparison with the figures given by these authors for binary mixtures of $C_{23}H_{46}O_2$ and $C_{25}H_{50}O_2$ suggests that the oxidation product contains at least traces of a third constituent.

It is interesting, further, that the *c* spacing measured on Klenk's phrenosinic acid is itself appreciably shorter than that recorded by Chibnall, Piper, and Williams on Dr. Rosenheim's preparation (55·4, 56·2 A.). This suggests that Klenk's preparation is more nearly pure $C_{24}H_{48}O_3$ and supports the contention raised by the above authors that the acid obtained from different sources may vary slightly in composition.

EXPERIMENTAL.

Phrenosinic Acid (*Klenk*).—The acid supplied by Klenk was too finely crystalline to allow direct single-crystal measurements to be obtained. Attempts were therefore made to recrystallise it from acetone and from benzene, but in both cases gel formation occurred, as described by Chibnall, Piper, and Williams. From benzene the effect was particularly striking, the whole solution after gentle warming setting immediately to a jelly on cooling.

By melting and recrystallisation under a heat gradient, sheets of phrenosinic acid could be obtained which appeared under the microscope to be single crystals. They showed a good extinction and in convergent light what appeared to be a rather poor positive biaxial figure slightly inclined to the plane of the sheet (001). The *X*-ray examination proved, however, that these crystals were invariably twins on (001) of two probably triclinic crystals with *a* axes inclined at an angle of about 19°. All the *X*-ray reflections were very much blurred, as would be expected from an impure substance, and accurate measurements were therefore impossible.

Oxidation Product of Phrenosinic Acid (*Klenk*).—By recrystallisation from acetone, this acid was obtained in very good, small, rhomb-shaped plates, showing the forms {001} (dominating) and {110} (Fig. 1). Through (001) a positive biaxial figure was observed with a very small optic axial angle, α along *b*, γ much inclined to (001). The unit cell dimensions (see table) show that the *B*-polymorphic type of fatty acid structure is present as measured by Muller for stearic acid, where $a = 5{\cdot}55$, $b = 7{\cdot}38$, and $c \sin \beta = 43{\cdot}76$ A. (*Proc. Roy. Soc.*, 1927, *A*, **114**, 535).

The density of the crystals was determined by flotation in very dilute zinc sulphate solutions, the centrifuge being used to hasten equilibrium. The value obtained was $1{\cdot}037 \pm 0{\cdot}003$, and this, combined with the cell dimensions, gives as the "molecular weight" of the acid present 364 ± 6 (Calc.: for $C_{24}H_{48}O_2$, 368; for $C_{23}H_{46}O_2$, 354). In the case of a mixture, the measurement might lose significance owing to variation among individual crystals. Such variation was not observed on the two different crystals examined.

FIG. 1.

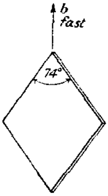
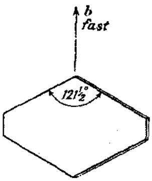


FIG. 2.



On melting and recooling, a second polymorphic modification could be obtained in sheets, which were approximately single crystals. A flake broken off gave from oscillation photographs about *a* the typical *C*-type spacings recorded in the table.

Tricosanoic Acid, $C_{23}H_{46}O_2$ (*Ashton, Robinson, and Smith*).—By slow cooling from solution in acetone, crystals of tricosanoic acid were obtained as large irregular flakes up to 2 mm. long. These proved to be triclinic, and therefore not to belong to either of the normal *B*- and *C*-types, though the axes may be chosen to show the relation of the structure with both of these. The direction of the fast extinction in the plane of the plate (001) lies along [010], which is also the direction along which the crystals are generally elongated; but the (010) plane most similar in intensity to (010) of the *B*-type is at angle of 73° to this direction. The cell dimensions given in the table show the close relation between this structure and the *B*-type. Further, in this cell *h0l* reflections do not appear for *h* odd.

On melting and then recooling these crystals, the *C*-modification first appears, but this is transformed exceedingly rapidly as the temperature falls, so that it was never possible to make *X*-ray or optical measurements on this variety at ordinary temperatures. In this, the behaviour of pure tricosanoic acid differs markedly from that of the oxidation product of phrenosinic acid, on which measurements of the *C*-form are easily obtainable. Such stabilisation of a metastable modification is, however, often produced by quite small traces of impurity (cf. picrates of the Diels hydrocarbon, Gamble, Kon, and Saunders, J., 1935, 644).

Lignoceric Acid, $C_{24}H_{48}O_2$ (*Ashton, Robinson, and Smith*).—Lignoceric acid crystallised from acetone in small rhomb-shaped plates showing the forms {001} (dominating), {100} (very small), and {110} (Fig. 2). The plane of the optic axes is (010), and γ is much inclined to the *c* face. The (200) reflection is very strong. Oscillation photographs were taken about *a*. This crystal modification is evidently the *C*-variety similar to that described by Brill and Meyer (*Z. Krist.*, 1928, **67**, 570) for lauric acid in which $a = 9{\cdot}76$, $b = 4{\cdot}98$, $c = 36{\cdot}9$, and $\beta = 48° 6'$. It is interesting that in this case the *C*- and not the *B*-variety has separated directly from solution (cf. Francis, Piper, and Malkin, *loc. cit.*).

Potassium Salts of Lignoceric and Tricosanoic Acids and of the Oxidation Product of Phrenosinic Acid.—The potassium salts were prepared by warming equivalent quantities of the acid and of potassium hydroxide together in alcoholic solution. With $C_{23}H_{46}O_2$, the acid potassium salt separated first, as proved by the *X*-ray measurements. This was subsequently converted into the normal salt.

The salt from the oxidation product of phrenosinic acid consisted of very poor, cloudy, minute crystals matted together so that they appeared to form plates. It was only possible to obtain a photograph to give the *c* spacing from a sample pressed on to a cover slip. The normal potassium salt of tricosanoic acid was photographed similarly for comparison.

The acid potassium salt of tricosanoic acid formed small, clear, lath-shaped crystals showing the (001) face with very small faces {100}, {210}, and elongated along [010]. The extinction is straight, the fast direction being along the needle axis. The *X*-ray measurements indicated the presence of an orthorhombic structure of some complication with the double layer of molecules probably placed lengthwise along *c*. Oscillation photographs were taken about the *a* and the *b* axis.

Substance.	Space group.	*n*.	*a*, A.	*b*, A.	*c*, A.	β.	d_{001}, A.	d_{010}, A.
Phrenosinic acid	$P1$	4	6·1	—	—	—	53·9	8·1
Oxidn. product of phrenosinic acid	*B* $P2_1/a$	4	5·57 ± 0·03	7·41 ± 0·03	—	—	56·50 ± 0·10	—
	C $P2_1/a$	4	9·0	5·0	65·8	128°	51·8	—
$C_{23}H_{46}O_2$	$P1$ or $P\bar{1}$	4	5·5	8·8	—	γ 73	53·1 (53·4)	7·5
$C_{24}H_{48}O_2$	*C* $P2_1/a$	4	9·0	4·97	66·5	127·5	52·8 (52·8)	—
K salt of oxidn. product	—	—	—	—	—	—	52·6	—
$C_{23}H_{45}O_2K$..................	—	—	—	—	—	—	51·7 (51·8)	—
$C_{23}H_{45}O_2K,C_{23}H_{46}O_2$ ...	*Cmmb*?	16	18·1	8·5	63·3	—	63·3 (63·25)	—
$C_{24}H_{47}O_2K$..................	$P1$ or $P\bar{1}$	2	5·6	4·2	65·4	124	54·2 (54·45)	—

Except where otherwise stated the measurements are not accurate to more than ±2%. Figures in parentheses are given for comparison from papers by Piper (J., 1929, 234) and Francis, Piper, and Malkin (*loc. cit.*).

The normal potassium salt of lignoceric acid also formed sufficiently good single crystals for measurement. These were very curious, curved, irregular plates, tending to be elongated along [110]. Through the plane of the plate (001) an optic eye is visible, part of a positive biaxial figure. The plane of the optic axes is (010), γ is much inclined to the *c* face. The crystals are probably triclinic, but can be given pseudomonoclinic axes. Oscillation photographs were taken about the *a* and the *b* axis.

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161. *Melting-point Curves of Optical Isomerides.*

By John D. M. Ross.

The melting-point curves of optical isomerides of certain substances in the camphor series have already been discussed (Ross and Somerville, J., 1926, 129, 2770), the conclusion being reached that acids and some esters were more likely to form racemic compounds than other substances. In the present instance attention was first directed to γγγ-trichloro-β-hydroxybutyric acid and its methyl ester, both of which could be obtained in a suitable form for the investigation of m.-p. curves, a condition which is common enough with esters, but not with acids. In extending the investigation to mandelic acid, it was hoped to be able to determine the form of the m.-p. curves of isomerides of the acid and of its methyl and ethyl esters. When mandelic acid was carefully melted in a m.-p. tube of the type already described (Ross and Somerville, *loc. cit.*), it did not give a definite m. p., but turned brown when molten, the smell of benzaldehyde being recognisable. Repeated melting gave increasing low m. p.'s. There was distinct evidence of decomposition, even when all possible precautions were taken to prevent the temperature rising much above the m. p., and so the attempt to determine the m.-p. curve of (—)- and (+)-mandelic acids was temporarily abandoned. Subsequent experiments showed that by a modification of the apparatus

it may be possible to determine more accurately the m. p.'s of mixtures of the acids. In previous investigations it was shown that the best criterion of purity of the isomerides was that they should have identical m. p.'s.

A further difficulty in determining the m.-p. curve of isomerides of mandelic acid is that the two forms of the acid are usually prepared by entirely different methods, as is the case here (see below), and are purified only by recrystallisation. This leads to the possibility that any impurity which may still be present in one isomeride will be a different impurity from that in the other. Differences in the physical properties of optical isomerides have been suggested in the case of mandelic acid, etc. (cf. Campbell and Garrow, *Trans. Faraday Soc.*, 1930, **26**, 560), but it seems likely that these results might be explained by the presence of traces of impurities in the isomerides. With mandelic acid, the decomposition at the m. p. and the difference in method of preparation of the two isomerides seriously affect the reliability of the results obtained.

Experimental.

Preparation of Optical Isomerides.—*r*-γγγ-Trichloro-β-hydroxybutyric acid was prepared by the interaction of chloral hydrate and malonic acid (von Auwers and Wissenbach, *Ber.*, 1923, **56**, 755), and resolved by means of quinine (McKenzie and Plenderleith, J., 1923, **123**, 1093), the yield of (−)-acid being much greater than that of the (+)-acid. The (−)-acid obtained had s. p. 99·9°, α − 0·64°, $[\alpha]_D^{17°}$ − 32·0° (l = 2, c = 1 in ethyl alcohol), and the (+)-acid s. p. 100·1°, $[\alpha]_D^{17°}$ + 32·0°; for the (−)-acid McKenzie and Plenderleith gave m. p. 104—105°, $[\alpha]_D^{17°}$ − 29·6°. The difference in the m. p.'s is accounted for by the different methods employed in the two cases, setting points being determined in the present instance, and the m. p. of the (−)-acid, when taken in the usual way, was 103°.

The methyl ester was prepared as follows. A solution of the acid (15 g.) in methyl alcohol (12 c.c.) was saturated with hydrogen chloride. After most of the alcohol had been removed under diminished pressure, the solution was again saturated with hydrogen chloride, the product poured into water, and extracted with ether. The ethereal solution was washed with potassium bicarbonate solution, the ether removed, and the product crystallised from light petroleum. In this way a (−)-ester of m. p. 58° and a (+)-ester of m. p. 60° were obtained. Further recrystallisation of both samples yielded substances melting at only slightly higher temperatures, and very little difference was observed in the specific rotations of the two forms of the ester. The difference in the setting points of the two isomerides pointed to the presence of impurities, and it was decided to try the effect of distillation under a high vacuum. By this treatment a (−)- and a (+)-ester, both of which had the same setting point, were obtained. The difficulty of getting pure samples of two optical isomerides is well illustrated in the present case, and the best test of purity seems to be the finding of identical setting points for the two forms of the isomeride.

Methyl (−)-*γγγ-trichloro-β-hydroxybutyrate* had m. p. 62·6°, α 0·75°, $[\alpha]_D^{17°}$ −37·5° (l = 2, c = 1 in ethyl alcohol), and the (+)-*methyl* ester had m. p. 62·6°, $[\alpha]_D^{17°}$ + 37·0° (Found: C, 27·1; H, 3·6; Cl, 48·0. $C_5H_7O_3Cl_3$ requires C, 27·1; H, 3·2; Cl, 48·0%).

Measurements of the conductivities of solutions of the racemic acid at 25° were made, in order to get values for comparison with the strength of known acids.

Concn.	*N*/8	*N*/16	*N*/32	*N*/64	*N*/128	*N*/256	*N*/512	*N*/1024
μ_v	9·95	14·50	21·51	28·92	40·44	55·49	75·34	105·2
m	0·0266	0·0388	0·0548	0·0773	0·1081	0·1484	0·2014	0·2811
$K \times 10^5$	9·08	9·76	9·95	10·12	10·23	10·09	9·02	10·74

This gives a value for the dissociation of the acid, $K = 10 \times 10^{-5}$, which is about twice that for benzoic acid.

(−)-Mandelic acid was prepared from amygdalin by treatment with hydrochloric acid, and the (+)-acid by resolving the inactive acid with cinchonine. After the acids had been so prepared, they were purified by repeated recrystallisation from benzene to which a small quantity of acetone had been added. The esters were prepared from the purest acid isomerides, obtained as above, by the Fischer–Speier method with sulphuric acid. After a number of recrystallisations from light petroleum, to which a drop or two of benzene had been added, the (−)- and the (+)-acid still had different m. p.'s. It was eventually found that the best method of purification was to distil the ester under a high vacuum, thereby removing traces of impurities. Finally, esters with the following properties were found: (−)-methyl mandelate had m. p.

54·4°, α − 2·44°, $[\alpha]_D^{16°}$ − 122° (l = 2, c = 1 in acetone), and the (+)-isomeride had m. p. 54·4°, $[\alpha]_D^{16°}$ + 124°; (−)-ethyl mandelate had m. p. 29·8°, α − 1·93°, $[\alpha]_D^{16°}$ − 96·5° (l = 2, c = 1 in acetone), and the (+)-ester had m. p. 29·8°, $[\alpha]_D^{16°}$ + 96·0°.

Determination of Setting Points.—The apparatus employed and the manner of determining the setting points were as already described (Ross and Somerville, *loc. cit.*). The temperatures were measured by means of a copper–constantan thermocouple, and in each case stirring was carried out by an electro-magnetic arrangement. Temperatures were checked with a standard thermometer, due allowance being made for the length of emergent stem.

γγγ-Trichloro-β-hydroxybutyric Acid and its Methyl Ester.

	Substances used for calibration.	Table and fig.	Remarks.
Acid	*m*-Dinitrobenzene (89·3°) Benzoic acid (121·9°)	I, 1	Setting point; acid seeded in each case; glycerol-bath for heating.
Ester	Urethane (45·7°) *p*-Bromophenol (62·6°)	II, 2	Setting point; ester seeded in each case; water-bath for heating.

TABLE I.

(+)-Acid, %.	S. p.	(+)-Acid, %.	S. p.
0·0	99·9°	50·0	118·3°
4·6	97·9	53·9	116·1
8·9	96·6	54·4	116·8
9·1	96·6	67·2	109·3
12·3	96·8	72·8	107·2
14·2	98·8	80·2	99·2
16·7	99·4	83·3	99·6
25·6	103·5	91·0	97·2
33·9	108·9	95·3	98·5
38·8	112·2	100·0	100·1
42·2	115·1		

TABLE II.

(+)-Ester, %.	S. p.	(+)-Ester, %.	S. p.	(+)-Ester, %.	S. p.
0·0	62·6°	41·6	58·0°	73·4	50·9°
5·6	59·2	41·8	57·7	76·0	49·8
10·4	56·9	50·0	58·8	78·7	48·0
16·3	51·7	53·1	58·5	78·9	48·4
22·1	48·6	57·3	58·3	82·0	50·4
22·2	48·3	62·3	57·2	85·6	52·5
25·2	49·6	65·6	55·6	89·7	56·2
27·8	51·9	65·8	55·8	94·5	58·8
28·0	52·3	68·1	55·1	100·0	62·6
35·8	56·1				

In the two foregoing cases the type of curve (Figs. 1 and 2) shows that a racemic compound has been formed.

FIG. 1.

γγγ-Trichloro-β-hydroxybutyric acid.

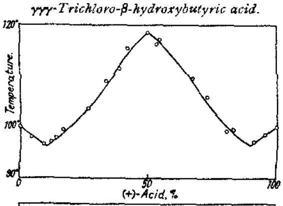
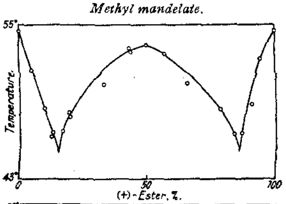


FIG. 3.

Methyl mandelate.



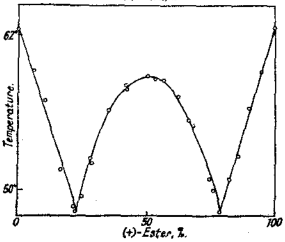


FIG. 2.

Methyl ester of γγγ-trichloro-β-hydroxybutyric acid.

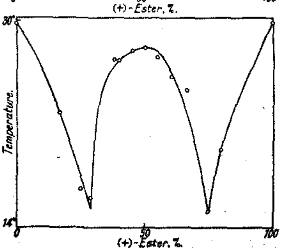


FIG. 4.

Ethyl mandelate.

In dealing with the esters of mandelic acid, hand stirring by means of a glass rod was used, and it was found more convenient to standardise the thermocouples as follows. The bulb of a standard thermometer was immersed in water, contained in the m.-p. tube, and the temperature of the thermometer, duly corrected for emergent stem, and the corresponding potentials were read off. M. p.'s were taken in each case, but in dealing with the ethyl esters special precautions were necessary, since in order to induce crystallisation they had to be cooled in ice-water. Under such conditions, the esters took up moisture from the air, and so gave a low m. p. It was, therefore, found essential to dry the esters in a desiccator between each determination of the m. p.

TABLE III.

Methyl mandelate.

(+)-Ester, %.	Temp.	(+)-Ester, %.	Temp.
0·0	54·4°	50·0	53·3°
4·8	51·2	57·0	52·6
9·1	48·5	66·1	50·3
13·0	46·1	78·8	48·4
13·0	46·4	83·7	46·7
16·7	46·5	87·2	46·8
20·0	48·2	91·1	48·8
20·0	47·9	95·3	52·0
33·3	50·2	100·0	54·4
42·9	52·8		

TABLE IV.

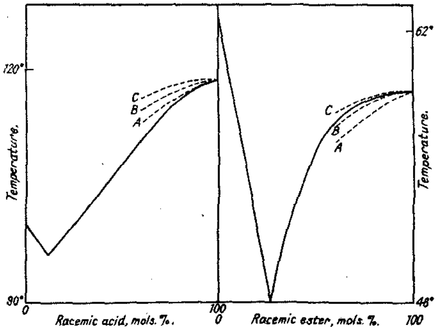
Ethyl mandelate.

(+)-Ester, %.	Temp.	(+)-Ester, %.	Temp.
0·0	29·8°	50·0	28·1°
16·7	22·9	(*r*-Ester)	28·0
25·0	17·0	54·4	27·2
28·6	16·1	60·0	25·8
33·3	24·4	66·7	24·7
37·5	27·1	75·0	15·2
40·0	27·1	80·0	20·1
45·4	27·7	100·0	29·8

In both cases the type of curve obtained (Figs. 3 and 4) shows that a racemic compound is formed.

Analysis of Experimental Curves.—The curves are symmetrical, and for purposes of analysis half of the experimental curves were drawn, the molar percentages of the racemate being plotted

FIG. 5. FIG. 6.



γγγ-Trichloro-β-hydroxybutyric acid. *Methyl ester of γγγ-trichloro-β-hydroxybutyric acid.*

against the m. p.'s. The shape of the curve near the m. p. of the racemate indicates the degree of dissociation of the racemic compound. If definite percentages of dissociation are assumed, Kremann (*Monatsh.*, 1904, **25**, 1215) has shown how the shape of the curve may be found. By using this criterion, the m. p.'s of the different mol.-fractions for γγγ-trichloro-β-hydroxybutyric acid were calculated for 10%, 15%, and 20% dissociation.

Curve.	Mol.-fraction (x) =	0·0.	0·2.	0·4.
A	t for 10%	118·3°	116·2°	112·6°
B	t for 15%	118·3	117·3	114·5
C	t for 20%	118·3	117·8	115·8

The curves A, B, and C are drawn in Fig. 5. The experimental curve lies near the curve A, and the dissociation of the racemate was taken to be 10%. Similar calculations for the other substances examined gave the following results:

Methyl γγγ-trichloro-β-hydroxybutyrate (see Fig. 6).

Curve.	Mol.-fraction (x) = 0·0.		0·2.	0·4.
A	t for 10%	58·8	57·8	56·1
B	t for 15%	58·8	58·3	57·0
C	t for 20%	58·8	58·5	57·6

Dissociation of racemic ester, 16%.

Methyl mandelate (see Fig. 7).

Curve.	Mol.-fraction (x) = 0·0.		0·2.	0·4.
A	t for 10%	53·3	52·1	50·1
B	t for 15%	53·3	52·7	51·1
C	t for 20%	53·3	53·0	51·9

Dissociation of racemic ester, 20%.

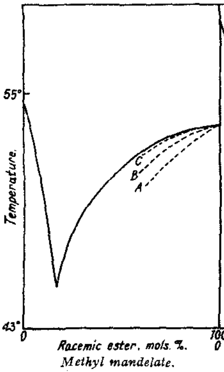
Ethyl mandelate (see Fig. 8).

Curve.	Mol.-fraction (x) = 0·0.		0·2.	0·4.
A	t for 10%	28·0	26·7	24·6
B	t for 15%	28·0	27·4	25·7
C	t for 20%	28·0	27·7	26·8

Dissociation of racemic ester, 20%.

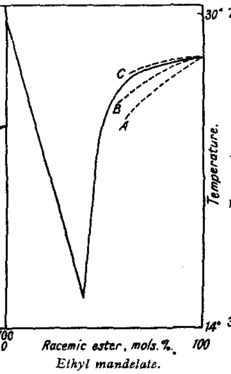
The degree of dissociation of the racemate may also be calculated by a formula worked out by van Laar, though, as Kremann has shown, the value so obtained is generally 2—3 times as

FIG. 7.



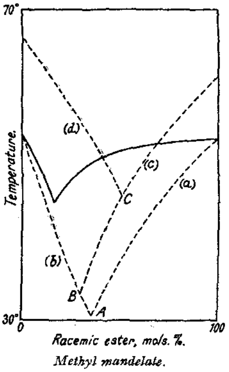
Methyl mandelate.

FIG. 8.



Ethyl mandelate.

FIG. 9.



Methyl mandelate.

great as that given by the graphical method. This observation has been confirmed in the present instances, and also for camphoric acid and methyl hydrogen camphorate (Ross and Somerville, *loc. cit.*). In some cases van Laar's formula gives values corresponding to almost complete dissociation of the racemate, a result which is not in conformity with the shape of the experimental curves. It is reasonable, therefore, to assume that the graphical method gives more reliable data for the degree of dissociation of the racemate.

Attempts have been made to apply the equation for "ideal solutions," *viz.*, $dT/dx = RT^2/Lx$, to the lowering of m. p. of optical isomerides. The values given by this equation have been

worked out in the case of methyl mandelate, and the results are shown in Fig. 9. If the above equation is applied directly to the lowering of the observed m. p. of the racemic and of the active ester [curves (*a*) and (*b*)] the eutectic point given by the intersection of these two curves (point *A*) is much lower than the observed eutectic. The main difficulty in the application of this equation is due to the dissociation of the racemic ester. If we take the value of the dissociation from Kremann's criterion, we can calculate what the m. p. of the undissociated racemate would be. The curve (*c*) would then show the lowering of the m. p. of the undissociated racemate, and the eutectic point would be the point *B*, which again is much lower than the observed eutectic point. It has been found, however, that when two active isomerides form a racemic compound the active forms are themselves associated. If we assume that the active forms are associated to the same extent as the (+)- and (—)-forms are associated in the racemic compound, we get curves (*c*) and (*d*) for the lowering of m. p., which give a eutectic point approximating closely to the observed value. The difference between the observed and the calculated eutectic percentage composition may be explained by the fact that the experimental curve is drawn for molar percentages of racemate and active ester. In the other cases investigated, the theoretical curves for "ideal solutions" give the best agreement with the observed eutectic temperature, though a difference is generally observed between the theoretical and the observed eutectic percentage composition.

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NOTES.

The "Activated Complex" Theory and the Influence of Solvents on Reaction Velocity.

By S. GLASSTONE.

THE "activated complex" or "transition state" theory of reaction velocity (Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492; Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875) leads to the conclusion that for a bimolecular reaction involving A and B, the reaction velocity in solution should be $f_A f_B / f_{AB^*}$ times as great as for the dilute gas, where the f terms represent the activity coefficients of A, B, and the activated complex AB*, respectively, in the given solution, the dilute gas being taken as the standard state. Since the activity coefficients may be assumed to be inversely proportional to the saturation solubilities (s), it follows that the above factor becomes $s_{AB^*}/s_A s_B$, and the velocity of the reaction in different solvents will be determined by this quantity. According to Hildebrand's theory ("Solubility," 1924) a normal solubility is observed, provided polarity and compound formation do not interfere, when the internal pressures of solvent and solute are similar, but if they differ the solubility will be lower than the ideal value. If, in the reaction under consideration, A and B have internal pressures of the same order as that of the solvent, whereas that of the activated complex AB* is different, it is evident that $s_{AB^*}/s_A s_B$ will be small. On the other hand, if the internal pressures of AB* and of the solvent are similar, but those of A and B different, the factor will be large. If it is assumed that the activated complex is related to the reaction product, as will probably be the case in a process of the type $A + B \longrightarrow AB$, *it follows that a solvent should facilitate a reaction if it* has an internal pressure of the same order as that of the product but different from that of the reactants, and should retard it if the reverse is the case. This conclusion is a generalised form of the empirical rules put forward by Richardson and Soper (J., 1929, 1873; see also Ingold and Jessop, J., 1930, 713; Soper and Williams, J., 1932, 2297). It may be noted that the activated-complex theory requires the entropy change of the process $A + B \longrightarrow AB^*$ to be related to the P factor in the expression $k = PZe^{-E/RT}$: Soper (J., 1935, 1393) has found a definite parallelism between P and the entropy change of the complete reaction $A + B \longrightarrow AB$, a result which suggests, as has been assumed above, that in many instances the activated complex resembles the product rather than the reactants.

A modification of Langmuir's vapour-pressure eqnation (*J. Amer. Chem. Soc.*, 1932, **54**, 2798) leads to the relationship $1/s = \alpha T^{\frac{1}{2}} e^{-\Delta H/RT}$ (cf. Wynne-Jones and Eyring, *loc. cit.*), where α is a constant for non-associated substances, and ΔH is the energy required to vaporise 1 g.-mol.

of solute from the particular solution. Where the solubility in different solvents depends only on differences in internal pressure, it is evident that in the expression for the velocity constant the P factor will not change, but E, which includes the ΔH terms, will vary, for a given reaction, from one solvent to another. Since association, either chemical or physical, and compound formation influence solubility, they should have an effect on reaction velocity. If the reactant molecules are associated in a particular solvent, but those of the activated complex are not, then that solvent will tend to give a high reaction velocity; association of the complex, but not of the reactants, should result in a less rapid reaction. In these instances the values of both α and ΔH vary in the expression for $1/s$, so there should be differences in both P and E when comparing velocity constants in different media. Compound formation between one or both the reactants and the solvent will result in increase of s_A or s_B or both, and so the reaction velocity will be diminished: in such circumstances the values of ΔH will be increased, and consequently there will be a corresponding increase in the apparent activation energy of the process (cf. Moelwyn-Hughes and Sherman, this vol., p. 101).

When the solvent is itself associated, the s terms for A, B, and AB* will all be affected, mainly because of changes in ΔH, but also perhaps because the α values are affected. It is not possible, however, to predict the influence of such a solvent on reaction velocity without consideration of the nature of the substances involved.—THE UNIVERSITY, SHEFFIELD. [*Received, February 28th*, 1936.]

A Further Resinol from Matai (Podocarpus spicatus). By LINDSAY H. BRIGGS and DOUGLAS A. PEAK.

AGREEING with Haworth, Richardson, and Sheldrick (J., 1935, 1576), we have obtained a further resinol, conidendrin, m. p. 254—255°, in very small amount from the mother-liquors of matairesinol from the wood of matai (*Podocarpus spicatus*) (for the second resinol, m. p. 212·5—213°, see Briggs, Peak, and Wooloxall, *Proc. Roy. Soc. N.S. Wales*, 1935, **69**, 61). This is of interest from a phytochemical point of view, since the constitutions of matairesinol (Easterfield and Bee, J., 1910, **97**, 1028; Haworth and Richardson, J., 1935, 633; Briggs, Peak, and Wooloxall, *loc. cit.*) and conidendrin (Holmberg, *Ber.*, 1921, **54**, 2389, 2406; *Ann. Acad. Sci. Fennicae*, 1927, *A*, **29**, No. 6; Erdtman, *Annalen*, 1934, **513**, 229; Haworth, Richardson, and Sheldrick, *loc. cit.*) have been shown to be closely related. We prefer the generic name conidendrin, suggested by Erdtman (*loc. cit.*), to the synonymous names sulphite-liquors lactone and tsugaresinol.

Conidendrin was obtained from the mother-liquors of matairesinol by digestion with insufficient alcohol for complete solution, filtration of the undissolved material, and its recrystallisation from 60% acetic acid and then twice from alcohol. It, alone or mixed with authentic conidendrin, had the characteristic m. p. recorded by Holmberg (*Ber.*, 1921, **54**, 2389): slow heating, m. p. 254—255° after shrinking at *ca.* 236°; quick heating, decomp. at *ca.* 236°, m. p. 254°; rapid heating, m. p. *ca.* 232°. With alcoholic ferric chloride it gives a green coloration, and with concentrated sulphuric acid and sodium nitrite a brownish colour, becoming red and finally blue (Found: C, 67·4; H, 5·6. Calc. for $C_{20}H_{20}O_6$: C, 67·4; H, 5·7%). In acetone (0·0532 g. in 5 c.c.) it had $[\alpha]_D^{14°}$ −47°. Holmberg records $[\alpha]_D^{20°}$ −54·7° and Emde and Schartner (*Helv. Chim. Acta*, 1935, **18**, 344) $[\alpha]_D^{20°}$ −54·8°.

The dimethyl ether, prepared from 150 mg. of the resinol according to Holmberg (*Ber.*, 1921, **54**, 2406), had m. p. 178·5—179°, undepressed by authentic dimethyl conidendrin (Found: C, 68·7; H, 6·0. Calc. for $C_{22}H_{24}O_6$: C, 68·7; H, 6·3%).

The microanalyses were made by Dr. G. Weiler. We are indebted to Dr. H. Erdtman for authentic specimens of conidendrin and derivatives and one of us (D. A. P.) acknowledges the award of a Duffus Lubecki Scholarship.—UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND. [*Received, March 5th*, 1936.]

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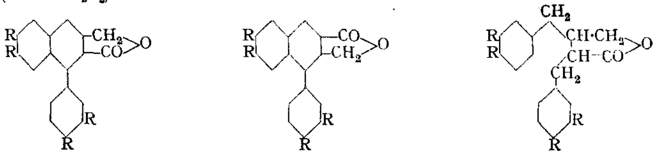
162. *The Constituents of Natural Phenolic Resins. Part V. Synthesis of* dl-*Matairesinol Dimethyl Ether and* dl-*Cubebinolide.*

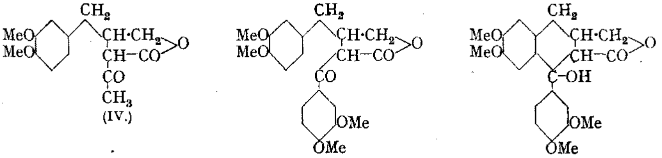
By Robert D. Haworth, William Kelly, and Thomas Richardson.

The synthetical work communicated in earlier parts of this series aimed at the preparation of lactones of types (I) and (II), but hitherto no method for the synthesis of lactones of type (III) has been recorded. The combination of reactive methylene groups with safrole oxide (this vol., p. 348) suggested a method for the preparation of lactones of this class, and the synthesis of *dl*-matairesinol dimethyl ether (III; R = OMe) and *dl*-cubebinolide (RR = CH_2O_2) is now described.



(I.) (II.) (III.)

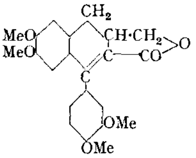
O-Methyleugenol oxide and ethyl sodioacetoacetate reacted in cold alcoholic solution to give *α-acetyl-β-(3 : 4-dimethoxybenzyl)butyrolactone* (IV). The constitution of this lactone was established by condensing the sodio-derivative with 3 : 4-dimethoxybenzoyl chloride, and converting the alkali-insoluble product into *α-(3 : 4-dimethoxybenzoyl)-β-(3′ : 4′-dimethoxybenzyl)butyrolactone* (V) by hydrolysis with cold dilute sodium hydroxide solution. Following the methods described in Part IV (*loc. cit.*), this lactone (V) was cyclised with methyl-alcoholic hydrogen chloride, and the *lactone* of *1-hydroxy-6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid* (VI) thus obtained was converted by dehydration into the *lactone* of *6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-3 : 4-dihydronaphthalene-2-carboxylic acid* (VII). Dehydrogenation of this dihydro-compound (VII) with lead tetra-acetate yielded the lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid (I; R = OMe), m. p. 254°, identical with the compound synthesised in Part II (J., 1935, 636) and the preparation of (I; R = OMe) by this new method establishes the structure of (IV).



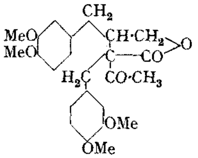
(IV.) (V.) (VI.)

After unsuccessful attempts had been made to convert (V) into (III; R = OMe) by applying the Clemmensen and the Wolff–Kishner process, the condensation of the sodio-derivative of (IV) and 3 : 4-dimethoxybenzyl chloride was investigated. *α-Acetyl-αβ-bis-(3 : 4-dimethoxybenzyl)butyrolactone* (VIII) was obtained as an alkali-insoluble oil, which on hydrolysis with methyl-alcoholic barium hydroxide yielded an acidic fraction from which *αβ-bis-(3 : 4-dimethoxybenzyl)butyrolactone* (dl-*matairesinol dimethyl ether*) (III; R = OMe), m. p. 106—107°, was obtained. The yield was extremely small, but the method, though of little preparative value, is of importance from the constitutional standpoint. An excellent method for the preparation of *dl*-matairesinol dimethyl ether has, however, been developed.

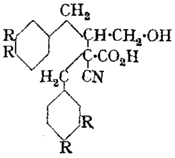
O-Methyleugenol oxide and methyl sodio-3 : 4-dimethoxybenzyl-α-cyanoacetate reacted in alcoholic solution, giving an acidic product which yielded a lactonic oil when warmed with dilute hydrochloric acid. This lactonic oil was converted into *dl*-matairesinol dimethyl



(VII.)

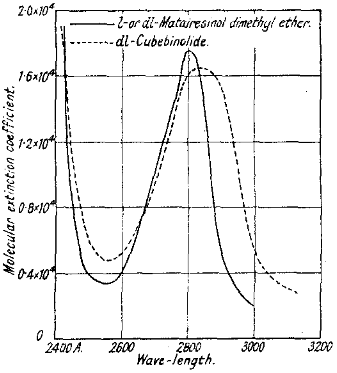


(VIII.)



(IX.)

ether, m. p. 106—107°, by boiling with concentrated hydrochloric acid, the overall yield being 36% of the theoretical. The nature of the acidic product mentioned above has not been investigated and such products have not been observed in similar reactions between



ethylene oxides and derivatives of ethyl acetoacetate or ethyl malonate. In view of the work of Thorpe (J., 1900, **79**, 923) on ethyl sodiocyanoacetate, the acidic product is probably (IX; R = OMe) and the lactonic oil may be the corresponding α-cyano-lactone. A further examination of these intermediate products is contemplated.

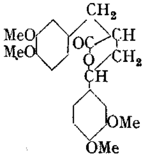
dl-Matairesinol dimethyl ether has been converted into *dibromo-*, *dinitro-*, and *tetranitro*-derivatives and the synthetic lactone and its derivatives closely resemble those of *l*-matairesinol dimethyl ether both in solubility in organic solvents and in colour reactions. The ultra-violet absorption spectra of *l*- and *dl*-matairesinol dimethyl ether are identical (fig.) and there can be little doubt that the natural and the synthetic product differ only in stereochemical configuration, but a rigid comparison must await a solution of the stereochemical problem. In Part I (J., 1935, 633) it was shown that lead tetra-acetate converted *l*-matairesinol dimethyl ether into a mixture of the dehydro-lactones (I; R = OMe) and (II; R = OMe), but this reaction does not occur with the *dl*-dimethyl ether. It is unlikely that this difference in behaviour is due to impurity in the natural matairesinol dimethyl ether, because repeated crystallisation does not affect the yield * of mixed

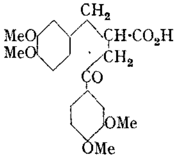
* The yield of mixed dehydro-lactones is approximately 10% as stated in Part I, p. 634; the amount recorded on p. 635 should be 0·05—0·08 g. instead of 0·5—0·8 g.

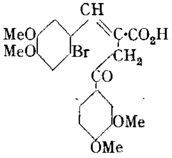
dehydro-lactones, and stereochemical factors are probably responsible for the discrepancy. In support of this opinion it may be recalled that stereoisomerides show marked differences in reactivity towards lead tetra-acetate. Criegee (*Ber.*, 1931, **64**, 360) showed that *cis*-glycols were attacked much more rapidly than the *trans*-isomerides, and in Part II (*loc. cit.*, p. 603) a similar difference was observed in the ease of dehydrogenation of the α- and the β-form of the lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid.

The dextrorotatory lactone, cubebinolide, was obtained by Mameli (see Part I for references) during his researches on cubebin, a constituent of the unripe fruit of *Piper cubeba*, and in 1922 the structure (III; RR = CH_2O_2) was advanced for the lactone. Later, Yoshiki and Ishiguro (*J. Pharm. Soc. Japan*, 1933, **53**, 11) examined Japanese hinokiresin and isolated a lævorotatory lactone, hinokinin, which they regarded as the enantiomorph of cubebinolide. This suggestion was supported by Keimatsu and Ishiguro (*ibid.*, 1935, **55**, 45), Briggs (*J. Amer. Chem. Soc.*, 1935, **57**, 1383), and Mameli (*Gazzetta*, 1935, **65**, 877, 886) and the formulation of cubebinolide as the methylenedioxy-analogue of matairesinol dimethyl ether led us to extend the scope of our experiments.

Safrole oxide and methyl sodio-3 : 4-methylenedioxybenzyl-α-cyanoacetate reacted in cold alcoholic solution, giving an alkali-soluble product, probably (IX; RR = CH_2O_2), which yielded an oily lactone when warmed with dilute hydrochloric acid. This lactonic oil was hydrolysed with concentrated hydrochloric acid and converted into αβ-*bis*-(3 : 4-*methylenedioxybenzyl*)*butyrolactone* (dl-*cubebinolide*) (III; RR = CH_2O_2), m. p. 106—107°, from which *dibromo*- and *dinitro*-derivatives have been prepared. The ultra-violet absorption of *dl*-cubebinolide (fig.) resembles that of *dl*-matairesinol dimethyl ether, but the absorption band is displaced in the direction of longer wave-length. While these experiments were in progress, Keimatsu, Ishiguro, and Nakamura (*J. Pharm. Soc. Japan*, 1935, **55**, 185) reduced αβ-bis-(3 : 4-methylenedioxybenzyl)succinic anhydride with amalgamated aluminium and obtained *dl*-hinokinin, m. p. 106—107°, probably identical with *dl*-cubebinolide described above. The absorption spectra of *dl*- and *l*-hinokinin are indistinguishable and are in harmony with our results for *dl*-cubebinolide. With the object of providing other methods of comparison, the dehydro-lactones (I; RR = CH_2O_2) and (II; RR = CH_2O_2) have been synthesised, but a description of this work is deferred until the completion of experiments, at present in progress, on the dehydrogenation of synthetic and natural cubebinolide.


(X.)


(XI.)


(XII.)

The compounds (X), (XI), and (XII) were prepared during unsuccessful preliminary experiments.

Experimental.

α-*Acetyl*-β-(3 : 4-*dimethoxybenzyl*)*butyrolactone* (IV).—*O*-Methyleugenol oxide (4·5 g.) (Fourneau and Tiffeneau, *Compt. rend.*, 1905, **140**, 1595; **141**, 662) was added to a solution of ethyl sodioacetoacetate (prepared from sodium, 0·5 g., and ethyl acetoacetate, 3·3 g.) in ethyl alcohol (20 c.c.). After 7 days water was added and neutral impurities were removed with ether. The alkaline liquor was acidified and extracted with benzene, and the solvent removed. Distillation of the residue gave an oil (4·5 g.), b. p. 218—220°/0·5 mm., which slowly solidified; it crystallised from benzene–light petroleum in colourless prisms (4 g.), m. p. 69—70°, which gave a purple ferric test (Found: C, 64·6; H, 6·6. $C_{15}H_{18}O_5$ requires C, 64·7; H, 6·5%).

α-(3 : 4-*Dimethoxybenzoyl*)-β-(3′ : 4′-*dimethoxybenzyl*)*butyrolactone* (V).—The lactone (IV)

(5·5 g.) was allowed to react with "molecular" sodium (0·5 g.) in benzene (20 c.c.) for 12 hours. 3 : 4-Dimethoxybenzoyl chloride (4·2 g.) was added and after 12 hours the mixture was refluxed for ½ hour. After addition of water, the separated benzene layer was washed with dilute sodium hydroxide solution and dried, and about half of the solvent removed. The residual benzene solution was diluted with ether (50 c.c.) and shaken with 5% sodium hydroxide solution (40 c.c.) for 7 hours. The *product*, liberated by acidification and isolated with chloroform, crystallised from methyl alcohol in colourless needles (2 g.), m. p. 125—126°, which slowly gave a green and later a purple colour with ferric chloride (Found : C, 66·3; H, 6·2. $C_{22}H_{24}O_7$ requires C, 66·0; H, 6·0%).

Lactone of 1-*Hydroxy*-6 : 7-*dimethoxy*-1-(3′ : 4′-*dimethoxyphenyl*)-3-*hydroxymethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylic Acid* (VI).—The lactone (V) (0·5 g.) was heated with methyl-alcoholic hydrogen chloride (15 c.c.) for 20 minutes, the mixture poured into water, the product extracted with chloroform, and the solvent removed. The residue crystallised from ether–light petroleum (b. p. 40—60°) in slender needles (0·3 g.), m. p. 124—126° (Found : C, 65·7; H, 6·1. $C_{22}H_{24}O_7$ requires C, 66·0; H, 6·0%), which gave no coloration with ferric chloride.

Lactone of 6 : 7-*Dimethoxy*-1-(3′ : 4′-*dimethoxyphenyl*)-3-*hydroxymethyl*-3 : 4-*dihydronaphthalene*-2-*carboxylic Acid* (VII).—The lactone (VI) (0·5 g.) was heated with potassium hydrogen sulphate (1·0 g.) at 180° for ½ hour. The *product*, isolated with chloroform, crystallised from methyl alcohol–chloroform in prisms (0·4 g.), m. p. 216—217° (Found : C, 68·8; H, 6·1. $C_{22}H_{22}O_6$ requires C, 69·1; H, 5·9%). This lactone (VII) (0·1 g.), lead tetra-acetate (0·2 g.), and glacial acetic acid (2 c.c.) were heated at 80° for 10 minutes. After dilution with water, the product, isolated with chloroform, crystallised from methyl alcohol–chloroform in colourless prisms (0·05 g.), which gave no depression in m. p. with a specimen of the lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid, m. p. 254°, prepared as described in Part II (*loc. cit.*).

α-*Acetyl*-αβ-*bis*-(3 : 4-*dimethoxybenzyl*)*butyrolactone* (VIII).—The sodio-derivative, prepared from (IV) (3·5 g.) as described above, 3 : 4-dimethoxybenzyl chloride (2 g.) (Tiffeneau, *Bull. Soc. chim.*, 1911, **9**, 928), and benzene (30 c.c.) were heated in a sealed tube at 100° for 18 hours. After washing, first with water and then with dilute sodium hydroxide solution, the benzene was removed, the residue distilled in a vacuum, and the fraction (1·5 g.), b. p. 270—280°/0·5 mm., collected (Found : C, 67·8; H, 7·0. $C_{24}H_{28}O_7$ requires C, 67·3; H, 6·6%). This viscous oil was insoluble in cold alkali and gave no colour with ferric chloride.

αβ-*Bis*-(3 : 4-*dimethoxybenzyl*)*butyrolactone* (dl-*Matairesinol Dimethyl Ether*) (III; R = OMe).—(a) The lactone (VIII) (1 g.) was boiled with 10% methyl-alcoholic barium hydroxide (10 c.c.) for 1 hour. Water was added, the methyl alcohol removed, the liquid filtered, and neutral impurities removed from the filtrate by extraction with chloroform. Excess of hydrochloric acid was added to the alkaline liquor and after boiling for 1·5 hours the product was extracted with chloroform and the extracts were washed thoroughly with sodium bicarbonate solution. Removal of the chloroform gave an oil, which slowly crystallised from aqueous methyl alcohol; the crystals were twice recrystallised from methyl alcohol (yield, 0·01 g.).

(b) *Methyl* 3 : 4-*dimethoxybenzyl*-α-*cyanoacetate*, prepared by heating the corresponding acid (Baker and Robinson, J., 1925, **127**, 1432) with 4% methyl-alcoholic hydrogen chloride (4 parts) for 4 hours, crystallised from methyl alcohol in colourless prisms, m. p. 75—76° (Found : C, 62·7; H, 6·0. $C_{13}H_{15}O_4N$ requires C, 62·65; H, 6·0%). *O*-Methyleugenol oxide (2·5 g.) was added to a cold solution of the above ester (3 g.) and sodium ethoxide (prepared from 0·3 g. of sodium) in absolute alcohol (30 c.c.), and the mixture kept for 3 days at room temperature. Water was then added, neutral impurities were removed in ether, the aqueous liquor was acidified and heated at 100° for 1 hour, and the oil which separated was isolated with ether. This nitrogenous oil, which was insoluble in aqueous sodium bicarbonate but slowly soluble in warm sodium hydroxide solution, was refluxed with concentrated hydrochloric acid (15 c.c.) for 4 hours. Water was added, the mixture extracted with chloroform, the extract washed with sodium hydroxide solution and dried, and the solvent removed; the residual oil was purified by a crystallisation from methyl alcohol (yield, 1·8 g.).

dl-*Matairesinol dimethyl ether*, prepared by method (a) or (b), separated from methyl alcohol in colourless slender prisms, m. p. 106—107° (Found : C, 68·2, 68·3; H, 6·6, 6·8. $C_{22}H_{26}O_6$ requires C, 68·4; H, 6·7%). It dissolved in concentrated sulphuric acid, giving an orange solution which became brown on addition of a drop of concentrated nitric acid. The statement made in Part I, p. 635, that *l*-matairesinol dimethyl ether gives a blue-green colour with concentrated sulphuric acid is incorrect; the reaction is identical with that described above for the *dl*-dimethyl ether.

dl-*Dibromomatairesinol dimethyl ether*, prepared by the addition of bromine (2 mols.) to *dl*-matairesinol dimethyl ether in glacial acetic acid, crystallised from methyl alcohol in colourless slender needles, m. p. 109—110° (Found: C, 48·5; H, 4·3. $C_{22}H_{24}O_6Br_2$ requires C, 48·5; H, 4·4%). It dissolved in concentrated sulphuric acid to a light brown solution, which became bright red on addition of a drop of concentrated nitric acid.

dl-*Dinitromatairesinol dimethyl ether*, prepared by the action of concentrated nitric acid (2 mols.) on the ether in glacial acetic acid, crystallised from methyl alcohol–chloroform in pale yellow needles, m. p. 179—180° (Found: C, 55·5; H, 5·2. $C_{22}H_{24}O_{10}N_2$ requires C, 55·4; H, 5·0%). With concentrated sulphuric acid it gave a bright red solution, which became orange on addition of a drop of concentrated nitric acid.

dl-*Tetranitromatairesinol dimethyl ether*, prepared by boiling *dl*-matairesinol dimethyl ether with concentrated nitric acid (15 parts) for 5 minutes, crystallised from methyl alcohol–chloroform in almost colourless plates, m. p. 185—186° (Found: C, 47·0; H, 4·0. $C_{22}H_{22}O_{14}N_4$ requires C, 46·6; H, 3·9%).

αβ-Bis-(3 : 4-methylenedioxybenzyl)butyrolactone (dl-*Cubebinolide*) (III; RR = CH_2O_2).—*Methyl 3 : 4-methylenedioxybenzyl-α-cyanoacetate*, prepared by heating the corresponding acid (Baker and Lapworth, J., 1924, 2336) with 4% methyl-alcoholic hydrogen chloride for 4 hours, crystallised from methyl alcohol in colourless prisms, m. p. 79—80° (Found: C, 62·0; H, 4·6. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·8%). Safrole oxide (4 g.) was added to a solution of the above ester (4 g.) and sodium ethoxide (from sodium, 0·4 g.) in absolute alcohol (50 c.c.), and the mixture kept for 3 days at room temperature. Water was then added, and the mixture was extracted with ether; the aqueous layer was acidified and heated at 100° for 1 hour and the nitrogenous lactone was isolated with ether and boiled with concentrated hydrochloric acid (20 c.c.) for 4 hours. After addition of water the mixture was extracted with chloroform, the extract washed several times with sodium hydroxide solution and dried, and the solvent removed; the residual oil crystallised from methyl alcohol in colourless prisms (1·0 g.), m. p. 106—107° (Found: C, 67·6; H, 5·1. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%). dl-*Cubebinolide* dissolved in concentrated sulphuric acid to a purple solution, which became red on addition of a drop of concentrated nitric acid.

dl-*Dibromocubebinolide*, prepared in glacial acetic acid solution, crystallised from alcohol in rhombic plates, m. p. 119—120° (Found: C, 46·8; H, 3·3. $C_{20}H_{16}O_6Br_2$ requires C, 46·9; H, 3·15%). It dissolved in concentrated sulphuric acid to a red-purple solution, which became brown on addition of a drop of concentrated nitric acid.

dl-*Dinitrocubebinolide*, prepared in acetic acid solution, crystallised from much alcohol or from ethyl acetate in stout, pale yellow prisms, m. p. 160—161° (Found: C, 54·0; H, 3·8. $C_{20}H_{16}O_{10}N_2$ requires C, 54·0; H, 3·6%). It gave with concentrated sulphuric acid a bright red solution, which became slightly paler on addition of concentrated nitric acid.

α-(3 : 4-Dimethoxybenzyl)-γ-(3′ : 4′-dimethoxyphenyl)butyrolactone (X).—The γ-lactone of β-(3 : 4-dimethoxybenzoyl)-α-(3′ : 4′-dimethoxybenzylidene)propionic acid (2 g.) (J., 1935, 636) in glacial acetic acid (150 c.c.) was shaken with hydrogen under a pressure of 95 pounds per square inch for 14 hours in presence of platinic oxide (0·05 g.). The *product* crystallised from methyl alcohol in colourless needles (1·5 g.), m. p. 126—127° (Found: C, 67·6; H, 6·4. $C_{21}H_{24}O_6$ requires C, 67·7; H, 6·4%). It is remarkable in view of the work of Jacobs and Scott (*J. Biol. Chem.*, 1930, **87**, 601) that the lactone ring does not undergo reductive fission.

β-(3 : 4-Dimethoxybenzoyl)-α-(3′ : 4′-dimethoxybenzyl)propionic Acid (XI).—The above lactone (0·4 g.) was dissolved in hot 5% methyl-alcoholic potassium hydroxide (10 c.c.), the methyl alcohol was removed, water was added, and potassium permanganate (0·1 g.) in water (25 c.c.) was gradually added. The manganese dioxide was removed, and the filtrate acidified; the *acid*, isolated with ether, crystallised from methyl alcohol in colourless needles, m. p. 107—108° (Found: C, 65·2; H, 6·3. $C_{21}H_{24}O_7$ requires C, 65·0; H, 6·2%).

β-(3 : 4-Dimethoxybenzoyl)-α-(2′-bromo-4′ : 5′-dimethoxybenzylidene)propionic Acid (XII).—The sodium salt of β-(3 : 4-dimethoxybenzoyl)propionic acid (2·6 g.), 2-bromo-4 : 5-dimethoxybenzaldehyde (3·6 g.), and acetic anhydride (12 c.c.) were heated at 100° for 2 hours; water was then added. The yellow *γ-lactone* crystallised from methyl alcohol–chloroform in orange needles, m. p. 202° (Found: C, 56·4; H, 4·3. $C_{21}H_{19}O_6Br$ requires C, 56·4; H, 4·3%). The lactone (3·2 g.) and sodium methoxide (from sodium, 0·16 g.) in methyl alcohol (25 c.c.) were refluxed for 1 hour. Water was added, the methyl alcohol removed, the filtered solution acidified, and the *acid* collected and crystallised from methyl alcohol–chloroform; colourless needles (2·8 g.), m. p. 225°, were obtained (Found: C, 54·3; H, 4·7. $C_{21}H_{21}O_7Br$ requires C, 54·2; H, 4·5%). The *methyl* ester, prepared by the action of methyl-alcoholic hydrogen

chloride, crystallised from methyl alcohol in felted needles, m. p. 140—141° (Found: C, 55·0; H, 4·9. $C_{22}H_{23}O_7Br$ requires C, 55·1; H, 4·8%).

Spectrographic Data.—Measurements were made with a Hilger medium quartz spectrograph. The light source was a condensed spark between tungsten-steel electrodes. The values are expressed as molecular extinction coefficients (ε). Approx. $M/10,000$ alcoholic solutions were used.

	$\lambda_{max.}$ A.	$\epsilon \times 10^{-4}$.
l-Matairesinol dimethyl ether	2,800	1·76
dl-Matairesinol dimethyl ether	2,800	1·76
dl-Cubebinolide	2,840	1·65

Our thanks are due to the Durham County Council Education Department for scholarships awarded to two of us (W. K. and T. R.).

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, March 31st, 1936.*]

163. *The Configuration of Heterocyclic Compounds. Part IV. The Optical Resolution of 10-Phenylphenoxarsine-2-carboxylic Acid.*

By MARY S. LESSLIE and E. E. TURNER.

IN Parts I and II (J., 1934, 1170; 1935, 1268) the resolutions of 10-methyl- and 10-ethylphenoxarsine-2-carboxylic acid were described. It was necessary to discover if the 10-aryl analogues could exhibit optical activity, and we therefore attempted the preparation of 10-phenylphenoxarsine-2-carboxylic acid. The synthetic method used for the alkyl compounds failed in the sense that treatment of 10-chlorophenoxarsine-2-carboxylic acid with phenylmagnesium bromide under various conditions gave no isolable quantity of the 10-phenyl acid. This difficulty was overcome by oxidising 10-phenyl-2-methylphenoxarsine (J., 1935, 1051) to 10-*phenylphenoxarsine*-10-*oxide*-2-*carboxylic acid* and reducing this, 10-*phenylphenoxarsine*-2-*carboxylic acid* being obtained.

Partial resolution of the 1-α-*phenylethylamine* salt of this acid took place readily in alcoholic solution. The complete resolution, which presented considerable difficulty, was accomplished with results which are summarised below (rotations in ethyl alcohol):

	M. p.	$[\alpha]^{20°}_{5791}$.	$[\alpha]^{20°}_{5461}$.
d-Acid	189—190°	+223·1°	+260·7°
dl-Acid	208—209	0	0
l-Acid	189—190	−223·2	−260·9

Attention is drawn to the high specific rotation of the new acid as compared with that of the methyl analogue, which has $[\alpha]^{20°}_{5791} \pm 96°$ in ethyl alcohol.

10-Phenylphenoxarsine has high optical stability. An ethyl-alcoholic solution of the *l*-acid lost none of its activity when it was heated for four hours in a closed tube at 100°. Oxidation of the *l*-acid to 10-phenylphenoxarsine-10-oxide-2-carboxylic acid was accompanied by complete loss of activity, although the oxide acid should be capable of optical activity even if the molecule is not possessed of a "folded" configuration. The resolution of the oxide acid is being attempted.

EXPERIMENTAL.

10-*Phenylphenoxarsine*-10-*oxide*-2-*carboxylic Acid.*—A suspension of 12 g. of 10-phenyl-2-methylphenoxarsine in a solution of 20 g. of potassium permanganate in 1200 c.c. of water was vigorously stirred at about 95° until oxidation ceased (1—2 hours). The resulting mixture was poured into excess of cold water saturated with sulphur dioxide and the *acid* precipitated was filtered off. It was dissolved in boiling alcohol, and excess of hot water added; 7 g. of small leaflets, m. p. 320°, then separated (Found: C, 60·0; H, 3·9. $C_{19}H_{13}O_4As$ requires C, 60·0; H, 3·45%).

dl-10-*Phenylphenoxarsine*-2-*carboxylic acid* was obtained by dissolving the oxide acid (19 g.) in chloroform, adding dilute hydrochloric acid and a little iodine, and passing sulphur dioxide

through the warmed mixture for about an hour, the chloroform being allowed to evaporate gradually but completely. The precipitated *acid* was collected and crystallised from alcohol, 14·5 g. of hexagonal plates, m. p. 206—207°, being obtained. Recrystallisation from benzene raised the m. p. to 208—209° (Found: C, 62·6; H, 3·7. $C_{19}H_{13}O_3As$ requires C, 62·65; H, 3·6%).

The acid separates from alcoholic solutions at 0—10° with alcohol of crystallisation, the product melting below 100° with loss of solvent of crystallisation. The sodium salt of the acid is sparingly soluble in aqueous sodium hydroxide, from which it can be caused to separate as leaflets.

Reduction of small quantities of the oxide acid may readily be effected without the use of chloroform, since it is appreciably soluble in dilute hydrochloric acid, no doubt as the hydroxychloride.

Resolution of 10-Phenylphenoxarsine-2-carboxylic Acid.—The acid (30 g.) and 10 g. of *l*-α-phenylethylamine were dissolved together in 1400 c.c. of hot ethyl alcohol. The solution was allowed to cool, the crystalline material removed, and the mother-liquor evaporated, this process being repeated so that six crops were obtained by successive reduction of the volume. The first (15·3 g.) had $[\alpha]_{5791}^{20°}$ +31·2° in methyl alcohol ($\alpha_{5791}^{20°}$ + 0·91°; l = 2; c = 1·458). The second (3·5 g.) had $[\alpha]_{5791}^{20°}$ − 27·1°; the third (6·5 g.) had $[\alpha]_{5791}^{20°}$ − 29·4°; the fourth (9·1 g.) had $[\alpha]_{5791}^{20°}$ − 18·9°; the fifth (0·7 g.) had $[\alpha]_{5791}^{20°}$ − 46·6°; and the sixth (0·6 g.) had $[\alpha]_{5791}^{20°}$ − 13·3°.

The first crop was recrystallised five times from ethyl alcohol, and 1·9 g. of salt were obtained with $[\alpha]_{5791}^{20°}$ + 184·3°. Further crystallisation did not alter this value.

Successive recrystallisations of the other crops gave salts, the specific rotations of which varied from + 12·2° to − 79·4°. By combining crops with approximately the same rotation and recrystallising them many times there was finally obtained a pure salt of the *l*-acid, with $[\alpha]_{5791}^{20°}$ − 191·2°.

l-α-*Phenylethylamine* d-10-*phenylphenoxarsine-2-carboxylate* crystallises from ethyl alcohol in clusters of needles, m. p. 208—209°, and has $[\alpha]_{5791}^{20°}$ + 184·3° and $[\alpha]_{5461}^{20°}$ + 214·5° in methyl alcohol (l = 2; c = 1·354; $\alpha_{5791}^{20°}$ = + 4·99°; $\alpha_{5461}^{20°}$ = + 5·62°) (Found: C, 67·1; H, 5·3. $C_{27}H_{24}O_3NAs$ requires C, 66·8; H, 5·0%).

l-α-*Phenylethylamine* l-10-*phenylphenoxarsine-2-carboxylate* crystallises from ethyl alcohol in very slender needles, m. p. 199—200°, and has $[\alpha]_{5791}^{20°}$ − 191·2° and $[\alpha]_{5461}^{20°}$ − 222·7° in methyl alcohol (l = 2; c = 1·441; $\alpha_{5791}^{20°}$ − 5·51°; $\alpha_{5461}^{20°}$ − 6·42°) (Found: C, 67·25; H, 5·2%).

The salts were decomposed by pouring a methyl-alcoholic solution into dilute hydrochloric acid, and the precipitated acids collected.

d-10-*Phenylphenoxarsine-2-carboxylic acid* crystallises in long glistening needles from ethyl alcohol. It melts at 189—190° and has $[\alpha]_{5791}^{20°}$ + 223·1° and $[\alpha]_{5461}^{20°}$ + 260·7° in ethyl alcohol (l = 2; c = 0·865; $\alpha_{5791}^{20°}$ = + 3·86°; $\alpha_{5461}^{20°}$ = + 4·51°) (Found: C, 62·5; H, 3·8%).

l-10-*Phenylphenoxarsine-2-carboxylic acid* has m. p. 189—190°, and $[\alpha]_{5791}^{20°}$ − 223·2° and $[\alpha]_{5461}^{20°}$ − 260·9° in ethyl alcohol (l = 2; c = 0·934; $\alpha_{5791}^{20°}$ − 4·17°; $\alpha_{5461}^{20°}$ − 4·875°) (Found: C, 62·1; H, 4·0%).

The *l*-acid was oxidised at room temperature with alkaline permanganate solution. A solution in aqueous ammonia of the oxide acid obtained was optically inactive.

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University of London (Bedford College). [*Received, April 4th, 1936.*]

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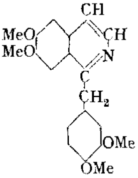
164. *a- and β-Hydroxylaudanosines. Part I. Their Preparation from Papaverinol.*

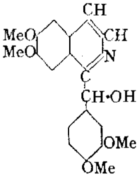
By F. E. King, Philibert L'Ecuyer, and F. L. Pyman.

Although the oxidation of papaverine (I) is usually accompanied by fission of the molecule, two products which retain the original benzyl*iso*quinoline skeleton have been described. These are the secondary alcohol (II) and the related ketone, and they correspond to successive stages in the oxidation of the methylene group. Papaveraldine, the ketone, was the first to be obtained (Goldschmiedt, *Monatsh.*, 1885, **6**, 954), and the alcohol, papaverinol, was at one time known simply as its reduction product (Stuchlik, *ibid.*, 1900, **21**, 813),

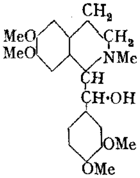
but a subsequent direct preparation of (II) from papaverine by the action of mercuric acetate (Gadamer, *Arch. Pharm.*, 1915, **253**, 274) definitely established it as an oxidation product of the alkaloid.



(I.)



(II.)



(III.)

On the other hand, in the parallel tetrahydropapaverine series, of which laudanosine is the most important example, the tendency to cleavage would appear to be appreciably greater (cf. Pyman, J., 1909, **95**, 1266), and oxidation products comparable with papaverinol and papaveraldine are unknown. Accordingly, with the ultimate intention of elucidating the mechanism of the oxidative scission of laudanosine, one of us (F. L. P.) several years ago undertook the reduction of papaverinol methochloride with the idea of preparing hydroxylaudanosine (*III*). Partly because the addition of hydrogen can create new asymmetric centres, several reduction products, *e.g.*, laudanosine and the stereoisomeric hydroxylaudanosines, *N*-methyl- and hydroxy-*N*-methyl-pavines, were possible. Tin and hydrochloric acid being used as reagents, actually three compounds were isolated, *viz.*, laudanosine, a hydroxylaudanosine, m. p. 138°, and a third base in the form of a *hydrochloride*, m. p. 231° (235° corr.).

The investigation was for a time interrupted at this juncture, but has lately been resumed and considerably simplified by adoption of the method of catalytic reduction. Under the new conditions the main product is the base, m. p. 138° (now designated *α-hydroxylaudanosine*), and by addition of hydrochloric acid to the alcoholic mother-liquors the hydrochloride, m. p. 231°, is obtained. This has been identified as a salt of a second or *β-hydroxylaudanosine*, m. p. 108—109°. No other products are formed during the reduction, and the isolation of the isomerides is therefore relatively simple, the total yield being nearly theoretical.

The two hydroxylaudanosines are now undergoing detailed investigation in a number of directions.

Experimental.

Papaverinol Methochloride.—Metho-salts of papaverinol were prepared by Stuchlik (*loc. cit.*, p. 824), who gives for the methiodide m. p., according to the rate of heating, 188—200°, and for the methochloride m. p. 178—182°, but no analysis. Papaverinol obtained by the method of Gadamer (*loc. cit.*) and recrystallised from alcohol until pure (m. p. 138°; yields, 50—70%) was refluxed with excess of methyl iodide for 4 hours; the methiodide obtained had m. p. varying from 185° to 210°. By digestion at 100° in aqueous-alcoholic solution with silver chloride it was converted into the *methochloride*, which crystallised from alcohol in colourless crusts of prisms, m. p. 205—206° (211—212° corr.) (Found: Cl, 8·6. $C_{21}H_{24}O_5NCl$ requires Cl, 8·7%).

Reduction of Papaverinol Methochloride.—(A) *The action of tin and hydrochloric acid.* A solution of the pure methochloride (48 g.) in alcohol (300 c.c.) was heated on a steam-bath with concentrated hydrochloric acid (100 c.c.) and tinfoil (20 g.). When the metal had dissolved, a second portion (20 g.) was added, together with a further quantity of acid (100 c.c.), and this was followed 2 hours later by a third portion (10 g.), after which the digestion was continued for another 4 hours. The product was then diluted with water, and the tin precipitated with hydrogen sulphide. The solution and washings were evaporated to dryness under reduced pressure, yielding a straw-coloured gum, which was dissolved in water, and after the addition of a slight excess of alkali, the solution was extracted with chloroform. The solvent was evaporated, and the extract (*ca.* 40 g.) dissolved in alcohol (35—40 c.c.) and left for 2 days to crystallise.

The solid which separated (9·6 g., m. p. *ca.* 130°) was contaminated with laudanosine, but crystallisation from 8—10 parts of alcohol gave pure *α-hydroxylaudanosine* (6·6 g.) as colourless stout needles, m. p. 138° (140° corr.) (Found : C, 67·5; H, 7·5. $C_{21}H_{27}O_5N$ requires C, 67·6; H, 7·2%).

The solution from which the crude hydroxylaudanosine had separated was mixed with oxalic acid (12 g.) and kept over-night; crystalline acid oxalates (21 g.) were then deposited. These were decomposed with aqueous sodium hydroxide, which was extracted first with ether and then with chloroform. From the ethereal solution, by evaporation and crystallisation from alcohol, laudanosine (3·2 g., m. p. 110—112°) was isolated, and by dissolving the evaporated chloroform extract in the alcoholic mother-liquor and allowing it to crystallise, a second crop (2·4 g., m. p. 100—102°, undepressed by authentic laudanosine) was recovered. The remaining alcoholic solution when evaporated to dryness yielded a gum, which on solution in a little fairly concentrated hydrochloric acid gave a hydrochloride (4 g.), *m.* p. 235° (corr.) after crystallisation from 5*N*-acid. A third specimen of laudanosine (1·9 g., m. p. 108°), which was isolated from the side fractions by means of the oxalate, was the only other crystalline product obtained in the course of the separation.

(B) *Catalytic hydrogenation.* Papaverinol methochloride (8 g.), dissolved in aqueous alcohol (30 c.c. of 70%), was reduced by means of hydrogen in the presence of platinum oxide catalyst (0·4 g.). After 4½ hours, when 2 molecules of hydrogen (*ca.* 490 c.c.) had been absorbed, reduction ceased. On filtration and evaporation to dryness under diminished pressure, the solution yielded a crystalline mass of hydrochlorides, which was treated with weak aqueous sodium hydroxide. The product was dissolved in boiling alcohol, and from the cooled solution there separated α-hydroxylaudanosine (5·6 g.), m. p. 136—137°, which afforded by one further crystallisation the pure substance, m. p. 138° alone or mixed with the specimen obtained as in (A).

A specimen of the base dissolved in the minimum amount of methyl alcohol was converted by the addition of alcoholic hydrogen chloride into *α-hydroxylaudanosine hydrochloride*, which crystallised from a small volume of alcohol in colourless prisms, m. p. *ca.* 135° (efferv.) (Found : C, 56·9; H, 7·3; Cl, 7·6. $C_{21}H_{27}O_5N,HCl,2H_2O$ requires C, 56·6; H, 7·2; Cl, 8·0%). The *picrate*, which was prepared by mixing equivalents of the two components in alcoholic solution, was only sparingly soluble in organic solvents. It was conveniently crystallised from dioxan, and formed light yellow prisms, m. p. 198° (decomp.) (Found : N, 9·3. $C_{21}H_{27}O_5N,C_6H_3O_7N_3$ requires N, 9·3%).

The alcoholic solution from which the α-hydroxylaudanosine had originally been crystallised was evaporated under diminished pressure. The syrupy residue showed no immediate tendency to crystallise, and it was therefore dissolved in alcohol (*ca.* 25 c.c.), to which a little alcoholic hydrogen chloride was then added. This caused the separation of *β-hydroxylaudanosine hydrochloride* (1·4 g.), which after a further crystallisation had m. p. 228—230° (efferv.). The pure salt crystallised from a moderate volume of alcohol in clusters of colourless needles, m. p. 231° (efferv.), and was identical with the material of m. p. 235° (corr.) isolated during the earlier experiment (Found : C, 61·2; H, 6·8; Cl, 8·5. $C_{21}H_{27}O_5N,HCl$ requires C, 61·5; H, 6·8; Cl, 8·7%).

An aqueous solution of the hydrochloride was basified, and the resulting white precipitate of *β-hydroxylaudanosine* was crystallised from aqueous alcohol (50%). The pure base formed a voluminous mass of minute needles which softened markedly at 74—75° and finally melted at 100° (efferv.), but after drying in an evacuated desiccator had m. p. 108—109° without previous softening (Found : C, 67·7; H, 7·4. $C_{21}H_{27}O_5N$ requires C, 67·6; H, 7·2%). Neutralisation with picric acid in alcoholic solution afforded the sparingly soluble *picrate*, which crystallised from methyl ethyl ketone in clusters of yellow prisms, m. p. 178—179° (Found : N, 9·4%).

In subsequent experiments a more active catalyst was used: not only was reduction more rapid, but the relative proportions of the two isomerides appeared to be affected. For example, the reduction of 125 g. of papaverinol methochloride, which required 13·8 l. of hydrogen, with the aid of 4·5 g. of catalyst, was complete within 1 hour, and on isolation of the products as already described, there were obtained 61 g. of pure α-hydroxylaudanosine and 40 g. of the β-isomeride, *i.e.*, a ratio of 2 : 1 as compared with 4 : 1 in the first experiment, and an overall yield exceeding 90%.

Thanks are due to the Rhodes Trustees for the award of a scholarship to one of us (P. L'E.), and to the Chemical Society for a grant.

The College of Technology, Manchester.
The Dyson Perrins Laboratory, Oxford.

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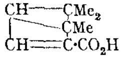
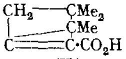
165. *α- and β-Camphylic Acids.*

By J. R. Lewis and J. L. Simonsen.

The products of the fusion of sulphocamphylic acid with alkaline hydroxides, examined first by Kachler (*Annalen*, 1872, **169**, 183) and Damsky (*Ber.*, 1887, **20**, 2957), formed the subject of a detailed investigation by Perkin, jun. (J., 1898, **73**, 829; 1903, **83**, 835). The main product of the fusion in the presence of reducing agents, such as are furnished by an iron pot, consists of *iso*lauronolic acid; if, however, the fusion is carried out in a nickel dish, the isomeric acids, α- and β-camphylic acids, $C_9H_{12}O_2$, are obtained. From a study of their reactions Perkin suggested that they were dicyclic unsaturated acids represented respectively by (I) and (II).


(I.)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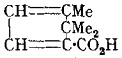
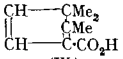
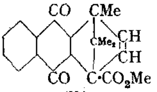

(III.)

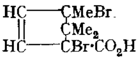

(IV.)

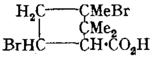
On stereochemical grounds it is obvious that the formula (II) suggested for β-camphylic acid is improbable, and a renewed study of these acids has shown α-camphylic acid to be *2 : 2 : 3-trimethyl-$\Delta^{3:5}$-cyclopentadiene-1-carboxylic acid (dehydro-α-campholytic acid)* (III) and β-camphylic acid to be 2 : 3 : 3-trimethyl-$\Delta^{1:4}$-*cyclo*pentadiene-I-carboxylic acid (dehydro*iso*lauronolic acid) (IV).

Before proceeding to discuss the evidence upon which the structure now advanced for these acids is based, we may refer briefly to their separation. We can confirm fully Perkin's statement that this is extremely laborious, more especially since the composition of the mixture varies considerably in different experiments. We find the relative proportion of the two acids formed to be dependent largely upon the pressure at which the product from the fusion is distilled. At the ordinary pressure or at pressures from 200—300 mm., α-camphylic acid predominates; the percentage of β-camphylic acid increases as lower pressures are used. In the latter case Perkin's method of separation by fractional steam distillation from the ammonium salts fails. If, however, an ethereal solution of the acids is fractionally extracted with ammonium carbonate solution, β-camphylic acid is preferentially removed and the residue can then be purified by Perkin's method. α-Camphylic acid is readily obtained pure by crystallisation from dilute acetic acid, but, in agreement with Perkin, we find that pure β-camphylic acid can only be prepared hy digestion of *iso*bromodihydro-β-camphylic acid with water.

Although on titration with percamphoric acid α-camphylic acid shows only the presence of one ethylenic linkage, two molecules of hydrogen are absorbed on catalytic hydrogenation with the formation of dihydro-α-campholytic acid, characterised by the preparation of the p-*phenylphenacyl* ester, m. p. 93°, identical with the same derivative obtained from the authentic *cyclo*pentane acid. On oxidation with ozone, α-camphylic acid yields methyl *iso*propyl ketone and oxalic acid, products which would result from the oxidation of an acid having the structure (III). Confirmation of the presence of a conjugated system of ethylenic linkages in the acid was obtained by the condensation of its methyl ester with α-naphthaquinone, the crystalline additive *compound* (V), m. p. 106°, being obtained.

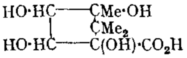

(V.)


(VI.)

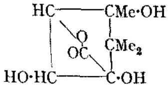

(VII.)

The structure now assigned to α-camphylic acid is not incompatible with the reactions of the acid as described by Perkin. It accounts for its reduction by sodium amalgam to α-campholytic acid, only the αβ-ethylenic linkage being reduced. With bromine the acid yields a dibromide, probably represented by (VI) (I : 4-addition), and the dihydrobromide

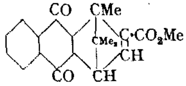
obtained by the action of hydrogen bromide may be (VII). It is less easy to account for the formation of the trihydroxy-acid, $C_9H_{14}O_5$, which Perkin prepared by the oxidation of α-camphylic acid with potassium permanganate in alkaline solution. It does not



(VIII.)



(IX.)



(X.)

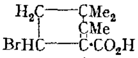
appear to us improbable that this substance was actually the lactone of the tetrahydroxy-acid (VIII), which would be the primary oxidation product of an acid (III). If the lactone be represented by (IX), it would account also for the fact that it only yields a monoacetyl derivative on acetylation, since two of the hydroxy-groups are tertiary.

In the light of the structure now assigned to α-camphylic acid it is of interest to note that it can be prepared also by the digestion of ethyl dibromodihydro*iso*lauronolate with diethylaniline. Since *iso*lauronolic acid is isomerised to α-campholytic acid by hydrobromic acid (Walker and Cormack, J., 1900, **77**, 378), it appears to us probable that the dibromo-ester used by Perkin was in reality ethyl dibromodihydro-α-campholate.

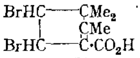
Proof of the structure of β-camphylic acid was obtained in a similar manner. Titration with percamphoric acid showed the presence of two ethylenic linkages and on catalytic hydrogenation a tetrahydro-acid was obtained, which was characterised by the preparation of the p-*phenylphenacyl* ester, m. p. 68—69°, and the amide, m. p. 160—161°. These were identical with derivatives prepared from authentic dihydro*iso*lauronolic acid. Oxidation with ozone gave methyl *iso*propyl ketone and oxalic acid, and with α-naphthaquinone the additive *compound* (X), m. p. 135°, was obtained from methyl β-campbylate, thus confirming the conjugation of the ethylenic linkages.

*iso*Bromodihydro-β-camphylic acid, which is prepared readily by the action of hydrogen bromide on crude β-camphylic acid, gives on ozonolysis an unstable bromo-acid, which after treatment with alkali is oxidised by sodium hypobromite to bromoform and *as*-dimethylsuccinic acid. This suggests that the cyclic acid is 5-bromo-2 : 3 : 3-trimethyl-Δ^1-*cyclo*pentene-1-carboxylic acid (XI).

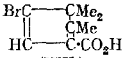
Like α-camphylic acid, the β-acid gives on bromination a dibromide. We have not prepared this substance, but, since hydrogen bromide attacks the Δ^4-linkage, we suggest that it is represented by (XII) and that bromo-γ-camphylic acid obtained from it by digestion with diethylaniline or acetic acid is (XIII) or (XIV).



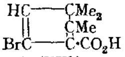
(XI.)



(XII.)



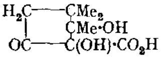
(XIII.)

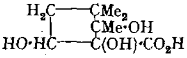


(XIV.)

It is more difficult on the basis of (IV) to account for the formation of the hydroxyketo-acid, $C_9H_{14}O_5$, obtained by Perkin by the oxidation of β-camphylic acid with potassium permanganate. This acid was assumed to be (XV), since it gave on further oxidation with chromic acid acetone and *as*-dimethylsuccinic acid. It is possible that hydration and oxidation occur simultaneously; (XVI) would then be the primary product. It is somewhat remarkable, in any case, that an acid having the structure (XV), which is that of a substituted acetoacetic acid, should be sufficiently stable to permit of its isolation.

(XV.)





(XVI.)

In view of the mobility of the ring system these experiments cannot be regarded as a contribution to the debated problem of the constitution of sulphocamphylic acid, and experiments on this are in progress.

EXPERIMENTAL.

α-Camphylic Acid.—In chloroform solution the acid reacted very slowly with percamphoric acid. After about 1 week, titration showed absorption of oxygen corresponding to one ethylenic linkage, and no change took place on further keeping.

Dihydro-α-campholytic Acid.—α-Camphylic acid was reduced in alkaline solution with hydrogen and a palladium-norit catalyst, complete rednction requiring approximately 24 hours. Acidification of the filtered solution, followed by extraction with ether, gave the dihydro-acid as an oil, which crystallised to a low-melting solid. This liquefied under water and was extremely readily soluble in the ordinary organic solvents. The p-*phenylphenacyl* ester crystallised from methyl alcohol in leaflets, m. p. 93° (Found: C, 79·0; H, 7·4. $C_{23}H_{26}O_3$ requires C, 78·9; H, 7·4%).

Oxidation of α-Camphylic Acid.—The acid (1 g.), dissolved in a mixture of carbon tetrachloride and ethyl acetate, was oxidised with ozone at 0°; no formaldehyde was detected in the issuing gases. After removal of the solvents under diminished pressure, the ozonide was decomposed in water (10 c.c.) on the water-bath. The solution, which contained a little resin in suspension, was distilled, the distillate having a strong odour of methyl *iso*propyl ketone. The *phenylsemicarbazone* crystallised from dilute methyl alcohol in needles, m. p. 101—102° (Found: N, 19·4. $C_{12}H_{17}ON_3$ requires N, 19·2%), unaltered on admixture with an authentic specimen (Found: N, 19·0%). The 2:4-dinitrophenylhydrazone crystallised from alcohol in yellow needles, m. p. and mixed m. p. 119—120° (Found: N, 21·3. Calc.: N, 21·1%). The residue in the distilling flask gave on evaporation oxalic acid, m. p. 100—101°.

Condensation of Methyl α-Camphylate and α-Naphthaquinone.—The methyl ester (0·35 g.), prepared by the action of diazomethane on the acid, and α-naphthaquinone (0·4 g.) in methyl alcohol (5 c.c.) were heated on the water-bath for 6 hours. Evaporation of the solvent left a brown solid which contained unchanged α-naphthaquinone. This was removed in steam and the gum which remained in the distilling flask was collected and crystallised from ligroin (b. p. 60—80°) (charcoal). The addition *product* separated in rosettes of needles, m. p. 106° (Found: C, 73·8; H, 6·4. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

β-Camphylic Acid.—The acid used in the experiments described below was purified through *iso*bromodihydro-β-camphylic acid. Preliminary experiments with an acid of the correct m. p. which had not been purified in this manner showed it to contain impurities leading to the formation of anomalous degradation products.

Interaction of β-camphylic acid with percamphoric acid in chloroform solution was rapid; addition of oxygen corresponding to one ethylenic linkage had occurred after 3 hours, and the reaction was complete in about 40 hours. A similar difference in the reactivity of the two ethylenic linkages was observed on hydrogenation in alkaline solution with a palladium-norit catalyst: 1 mol. of hydrogen was absorbed in 3 minutes, but complete reduction required 24 hours. The acid, dihydro*iso*lauronolic acid, so obtained, which was an oil, gave a p-*phenylphenacyl* ester crystallising from ligroin (b. p. 40—60°) in prisms, m. p. 68—69° (Found: C, 79·3; H, 7·4. $C_{23}H_{26}O_3$ requires C, 78·9; H, 7·4%). The amide prepared from the acid chloride had m. p. 160—161°.

Oxidation of β-Camphylic Acid.—The acid (1 g.) was ozonised in carbon tetrachloride solution at 0°, and the ozonide decomposed with water in the usual manner. Distillation of the aqueous solution gave methyl *iso*propyl ketone (2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 119—120°) (Found: N, 21·5. Calc.: N, 21·1%). The aqueous residue from the steam distillation gave on evaporation oxalic acid, m. p. 99—100°.

Condensation of Methyl β-Camphylate and α-Naphthaquinone.—This condensation was carried out under conditions similar to those used in the case of the ester from the α-acid, the yield being quantitative. The addition *product*, recrystallised from ligroin (b. p. 40—60°) (charcoal) and finally from *cyclo*hexane, was obtained in rosettes of needles, m. p. 135° (Found: C, 73·9; H, 6·3. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

Oxidation of iso*Bromodihydro-β-camphylic Acid.*—The acid (1 g.) was ozonised in ethyl acetate solution at 0°; after removal of the solvent the product was decomposed by hot water. Evaporation of the water in a vacuum left an oil, which partly crystallised, decomposition with evolution of hydrogen bromide gradually occurring. The oil was dissolved in sodium hydroxide solution (10%) and heated on the water-bath for 1 hour, and the cooled solution treated with an excess of sodium hypobromite at 0°; bromoform then separated. This was removed, the excess of hypobromite destroyed by sulphur dioxide, and the solution acidified and extracted with ether. Evaporation of the solvent gave an oil (0·6 g.) which crystallised when stirred with

hydrochloric acid. The acid, m. p. 130°, was purified through its sparingly soluble calcium salt; the recovered acid, after recrystallisation from water, had m. p. 139—140°, both alone and in admixture with *as*-dimethylsuccinic acid.

We are indebted to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Ltd. for grants.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, April 23rd, 1936.*]

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166. *Studies in the Sterol Group. Part XXII. 3-Chloro*allo*norcholanic Acid and its Epimeride.*

By T. BARR, I. M. HEILBRON, and F. S. SPRING.

IN an attempt to define the position of the hydroxyl group in ergosterol, Heilbron, Samant, and Simpson (J., 1933, 1410) oxidised chloroergostane to a chloro*allo*norcholanic acid, m. p. 213° (methyl ester, m. p. 158—159°), which was not identical with the 3-chloro*allo*norcholanic acid, m. p. 232—234° (methyl ester, m. p. 176°), prepared by these authors by degradation of 3-chloro*allo*cholanic acid (Windaus and Hossfeld, *Z. physiol. Chem.*, 1925, **145**, 177). This result meant that either the hydroxyl group of ergosterol is not attached to C_3 or an epimerisation had occurred during the chlorination of either cholesterol or ergostanol.

Subsequently Fernholz and Chakravorty (*Ber.*, 1934, **67**, 2021) produced conclusive proof that the hydroxyl group of ergosterol is attached to C_3, a property possessed by all naturally occurring sterols and bile acids that have so far been examined in detail. It follows that the chloro*allo*norcholanic acid of Heilbron, Samant, and Simpson must be a 3-chloro*allo*norcholanic acid, differing from that prepared by degradation of the Windaus and Hossfeld 3-chloro*allo*cholanic acid solely in the orientation of the groups attached to C_3.

It is to be noted that two isomeric 3-chlorocholestanes exist, namely, α-cholestyl chloride, m. p. 115° (Windaus and Hossfeld, *loc. cit.*), and β-cholestyl chloride, m. p. 105° (Ruzicka, Goldberg, and Brüngger, *Helv. Chim. Acta*, 1934, **17**, 1389). Of these, the latter is probably the *trans*- and the α-isomeride the *cis*-form (Ruzicka, Wirz, and Meyer, *ibid.*, 1935, **18**, 998; the terms *cis*- and *trans*- refer here to the orientation of the chlorine atom with respect to the hydrogen atom attached to C_5).

Since the 3-chloro*allo*norcholanic acid of Heilbron, Samant, and Simpson was prepared from α-cholestyl chloride, we have repeated the degradation, employing β-cholestyl chloride. We find that the 3-chloro*allo*norcholanic acid so obtained is identical with that previously prepared from chloroergostane. Depending upon the value of the melting point characterisation of α- and β-cholestyl chlorides, this 3-chloro*allo*norcholanic acid obtained from chloroergostane and β-cholestyl chloride is the *trans*- and that from α-cholestyl chloride the *cis*-isomeride. It will be noted that this decision again agrees with the melting point rule.

EXPERIMENTAL.

(trans ?)-3-*Chloro*allo*cholanic acid* from β-cholestyl chloride has previously been described by Ruzicka, Goldberg, and Brüngger (*loc. cit.*), but, as these authors anticipated, their product (m. p. 186—188°) was not pure; furthermore, it was not analysed or characterised. By repeated crystallisation from ether–light petroleum (b. p. 40—60°) the pure acid was obtained *in* plates, m. p. 195—196° (Found: C, 72·1; H, 9·6; Cl, 9·4. $C_{24}H_{39}O_2Cl$ requires C, 72·3; H, 9·9; Cl, 9·0%).

Methyl (trans ?)-3-*chloro*allo*cholanate*, prepared from the acid by means of diazomethane, separated from ether–methyl alcohol in flat needles, m. p. 134—135° (Found: C, 73·6; H, 10·0; Cl, 9·0. $C_{25}H_{41}O_2Cl$ requires C, 73·4; H, 10·0; Cl, 8·7%).

Methyl (trans ?)-3-*Chloro*allo*norcholanate*.—An ethereal solution of methyl (*trans* ?)-3-chloro*allo*cholanate (1·2 g.) was added to a Grignard solution of magnesium (0·26 g.), bromobenzene (1·5 g.), and ether (100 c.c.), and the mixture heated under reflux for 4 hours. The ether was

removed and the residue was heated on the steam-bath for a further 4 hours, decomposed with cold dilute sulphuric acid, and set aside over-night. The diphenylcarbinol was extracted with ether and isolated in the usual manner. It formed a pale yellow resin, which showed no tendency to crystallise from the common solvents and was therefore directly oxidised in glacial acetic acid solution (50 c.c.) with a solution of chromic anhydride (2·2 g.) in acetic acid (20 c.c. of 95%), added during 2 hours, and the heating was continued for a further 2 hours, mechanical stirring being applied throughout. After dilution with water the solution was extracted with ether, and the ethereal extract washed with water. On addition of potassium hydroxide solution (10%) the potassium salt of the 3-(*trans* ?)-chloro*allo*norcholanic acid was precipitated and isolated by centrifuging. The 3-(*trans* ?)-chloro*allo*norcholanic acid, obtained as an oil, was converted into its methyl ester with diazomethane, which after repeated crystallisation from ether–methyl alcohol separated in plates, m. p. 157—158°, giving no depression on admixture with methyl chloro*allo*norcholanate from chloroergostane (Found: C, 72·5; H, 9·34; Cl, 9·4. Calc. for $C_{24}H_{39}O_2Cl$: C, 72·9; H, 9·9; Cl, 9·0%). Hydrolysis of the ester was accompanied by partial removal of chlorine.

Our thanks are due to the Governors of the Royal Technical College, Glasgow, for a Scholarship which enabled one of us (T. B.) to participate in this investigation, also to Dr. K. M. Samant for help in the experimental section.

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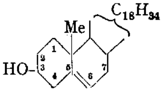
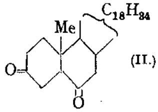
167. *Studies in the Sterol Group. Part XXIII. The Location of the Ethenoid Linkage of α-Dihydrofucosterol and the Identity of Sitostanol, Fucostanol, Stigmastanol, and Ostreastanol.*

By D. H. COFFEY, I. M. HEILBRON, and F. S. SPRING.

IT was recorded in Part XX that the hydrogenation of fucosteryl acetate in presence of a palladium catalyst gives a mixture of α- and β-dihydrofucosteryl acetates (Coffey, Heilbron, Spring, and Wright, J., 1935, 1205).

The oxidation of α-dihydrofucosterol with perbenzoic acid has now been found to give *α-dihydrofucosterol oxide,* also obtained by similar oxidation of α-dihydrofucosteryl acetate, followed by hydrolysis with sodium methoxide. Treatment of the α-oxide with sulphuric acid gives *α-fucostanetriol,* which is also formed by the action of hydrogen peroxide upon α-dihydrofucosterol. Chromic acid oxidation of α-fucostanetriol yields *α-fucostanedionol,* demonstrating that an ethenoid linkage of the type >C=CH— is present in α-dihydrofucosterol. This dionol is readily dehydrated by means of hydrogen chloride in chloroform to *α-fucostenedione,* which on reduction is converted into *α-fucostanedione* giving a pyridazine derivative, the formation of which proves the diketone to be fucostane-3 : 6-dione (II). It therefore follows that, as in the case of cholesterol (Windaus, *Z. physiol. Chem.*, 1933, **213**, 147) and stigmasterol (Fernholz, *Annalen*, 1934, **508**, 215), α-dihydrofucosterol (I) contains an ethylenic linkage between C_5 and C_6.

(I.) 

 (II.)

Confirmation of the relative positions of the hydroxyl group and the ethenoid linkage in α-dihydrofucosterol (I) has been obtained from an examination of α-fucostenone,* m. p. 81—82°, prepared by oxidation of dibromo-α-dihydrofucosterol, followed by debromination.

* The "α-fucostenone," m. p. 158°, previously described by Coffey, Heilbron, Spring, and Wright (*loc. cit.*) and prepared by the *direct* chromic acid oxidation of α-dihydrofucosterol, is a mixture containing α-fucostenedione together with unidentified products.

α-Fucostenone exhibits the typical absorption spectrum of an αβ-unsaturated ketone (Menschick, Page, and Bossert, *Annalen*, 1932, **495**, 225), from which it follows that during the oxidation of α-dihydrofucosterol the $\Delta^{5:6}$-ethylenic linkage has migrated to the $\Delta^{4:5}$-position, a transformation which has its exact parallel in the oxidation of cholesterol to cholestenone (Windaus, *loc. cit.*).

A comparison of stigmastanol and sitostanol (both natural dihydrositosterol and the hydrogenated sterol from tallöl) has led Bengtsson (*Z. physiol. Chem.*, 1935, **237**, 46) to postulate their identity. The conclusion of Heilbron, Phipers, and Wright (J., 1934, 1572) that stigmastanol and fucostanol are identical is criticised by this author on the grounds of the fallibility of the mixed melting-point test and also because of the low rotation previously recorded for fucostanol. We have again compared the physical characteristics of a variety of derivatives of fucostanol with those of corresponding derivatives of stigmastanol. This comparison clearly confirms the identity of fucostanol and stigmastanol. Furthermore, Bergmann (*J. Biol. Chem.*, 1934, **104**, 317, 553) records that the

	Fuco *		Stigma *		
	M. p.	$[\alpha]_D$.	M. p.	$[\alpha]_D$.	
-stanol	134·5—135—136° †	+24·7°	135·4—136·4—137°	+24·8°	(1)
-stanyl acetate	128—129—130	+15·1	128—129·8—131·2	+15·3	(1)
-stanyl 3 : 5-dinitrobenzoate	214—215	+13·8 (in C_6H_6)	208—214—215	+13·1 (in C_6H_6)	(1)
-stanyl benzoate	135—136	—	133—135·4—137·2	—	(1)
-stanone	156·5—157	+40·2	151—157—157·4	+40·6	(1)
-stanone oxime	217—218	+30·1	219	+30	(2)
-stanedicarboxylic acid	227—229	—	229—230	—	(3)
epi-stanol	200	+25·5	200	+25	(2)
epi-stanyl acetate	87	+27·4	85	+27	(2)

* All rotations, except where otherwise stated, are for chloroformic solution.

† Where three temperatures are recorded, they represent preliminary softening, melting to a cloudy liquid, and clearing.

(1) Bengtsson, *loc. cit.* (2) Dalmer, Werder, Honigmann, and Heyns, *Ber.*, 1935, **68**, 1814. (3) Windaus and Brunken, *Z. physiol. Chem.*, 1924, **140**, 47.

fully hydrogenated ostreastanol is identical with sitostanol; the interesting fact thus emerges that the characteristic sterols of molluscs, algae, and of the vegetable kingdom have a common carbon skeleton. In this connection, however, it is to be observed that γ-sitostanol differs from stigmastanol (Bonstedt, *Z. physiol. Chem.*, 1928, **176**, 269).

Sitosterol of wheat-germ oil has been shown to contain its ethylenic linkage between C_5 and C_6 (Pickard and Yates, J., 1908, **93**, 1928; Fernholz, *Annalen*, 1934, **508**, 215) and must therefore be identical with α-dihydrofucosterol. In view of the heterogeneity of sitosterol and the great variation in the literature regarding its constants and those of its acetate (Anderson *et alia*, *J. Amer. Chem. Soc.*, 1924, **46**, 1450, 1717; 1926, **48**, 2972; Bonstedt, *loc. cit.*; Ichiba, *Inst. Phys. Chem. Res.*, *Tokyo*, 1935, **28**, 112) a comparison is difficult. The table below, however, shows the striking similarity in the melting points of corresponding derivatives of the two series and leads us to the opinion that α-dihydrofucosterol is identical with $\Delta^{5:6}$-sitosterol, which has not hitherto been isolated free from isomeric contaminants.

	α-Fuco	Sito		α-Fuco	Sito
-stenol (1)	136—137°	138°	-stanedione (1)	192—194°	196°
-stenyl acetate (1)	133—134	134	,, pyridazine deriv. (1)	200	107—200
-stanetriol (1)	248—250	252	-stenone (2)	81—82	81—82
-stanedionol (1)	256	256	,, -semicarbazone (2)	250	254
-stenedione (1)	166	166 (129°)			

(1) Fernholz, *loc. cit.*; Pickard and Yates, *loc. cit.* (2) Heiduschka and Gloth, *Arch. Pharm.*, 1915, **253**, 415.

Experimental.

α-Dihydrofucosterol Oxide.—α-Dihydrofucosterol (1·0 g.) in chloroform (30 c.c.) was treated at —5° during 30 minutes with a chloroformic solution of perbenzoic acid (1·1 atom O). After

remaining at 0° for 24 hours, the solvent was removed, and the crude oxide dissolved in ether and washed with aqueous sodium carbonate. The *oxide* recovered from the ether separated from methyl alcohol in needles of constant m. p. 134°, $[\alpha]_D^{20°}$ − 35·6° (l = 1, c = 6·94 in chloroform) (Found: C, 80·5; H, 11·6. $C_{29}H_{50}O_2$ requires C, 80·8; H, 11·6%).

α-Dihydrofucosteryl acetate oxide, prepared by acetylation of the oxide or by oxidation of α-dihydrofucosteryl acetate with perbenzoic acid, separated from methyl alcohol in clusters of needles, m. p. 141° (Found: C, 78·7; H, 11·3. $C_{31}H_{52}O_3$ requires C, 78·8; H, 11·0%).

α-Fucostanetriol.—(a) α-Dihydrofucosterol oxide (1·0 g.) in glacial acetic acid (17·5 c.c.) was treated with two drops of concentrated sulphuric acid, the whole being maintained at 16° for 16 hours. The solution was diluted with water and extracted with ether, and the extract washed free from acetic acid. After removal of the ether the residue was hydrolysed by refluxing for 2 hours with alcoholic potash (100 c.c.; 5%), and the product isolated by water precipitation. α-Fucostanetriol separated from methyl alcohol in needles, m. p. 248—250°.

(b) A solution of α-dihydrofucosteryl acetate (10 g.) in glacial acetic acid (50 c.c.) was treated with hydrogen peroxide (Merck's perhydrol, 10 c.c.) and maintained for 1 hour at 100°. The solid separating from the cooled solution was directly hydrolysed with alcoholic sodium methoxide, and the product isolated by water precipitation, followed by crystallisation from methyl alcohol, from which *α-fucostanetriol* separated in needles, m. p. 248—250° alone or in admixture with that obtained by method (a) (Found: C, 77·5; H, 11·9. $C_{29}H_{52}O_3$ requires C, 77·6; H, 11·7%).

α-Fucostanedionol.—α-Fucostanetriol (1·0 g.) in glacial acetic acid (50 c.c.) was oxidised at room temperature with a solution of chromic anhydride (1·0 g.) in water (2 c.c.) and glacial acetic acid (8 c.c.), added during 3 hours. The solution was then stirred for 2 hours, diluted with water, and extracted with ether. The neutral portion, isolated from the extract in the usual manner, separated from methyl alcohol in needles, which after several recrystallisations from the same solvent had m. p. 256° (Found: C, 78·5; H, 10·8. $C_{29}H_{48}O_3$ requires C, 78·5; H, 10·9%).

Active-hydrogen determination (Zerewitinoff method).* 9·077 Mg. of fucostanedionol evolved 0·46 c.c. of methane at 20° and 0·48 c.c. of methane at 95°, corresponding to 1·006 and 1·05 atoms of active hydrogen per mole respectively.

α-Fucostenedione.—A solution of α-fucostanedionol (0·3 g.) in chloroform (30 c.c.) was treated for 1 hour with a rapid stream of hydrogen chloride. After washing with sodium carbonate solution, the chloroform was removed under reduced pressure, and the residue taken up in methyl alcohol, from which *α-fucostenedione* separated in needles, m. p. 166° (Found: C, 81·3; H, 10·8. $C_{29}H_{46}O_2$ requires C, 81·6; H, 10·9%).

α-Fucostanedione.—A solution of α-fucostenedione (0·3 g.) in acetic acid (10 c.c., 90%) was refluxed for 4 hours with zinc dust (0·3 g.). The excess of zinc was removed, the clear solution precipitated with water, and the solid collected. After several crystallisations from methyl alcohol *α-fucostanedione* separated in needles of constant m. p. 192—194° (Found: C, 81·1; H, 11·2. $C_{29}H_{48}O_2$ requires C, 81·2; H, 11·3%). The *pyridazine* derivative separated from chloroform–ethyl alcohol in needles, m. p. 200° (Found: C, 81·85; H, 11·3; N, 6·5. $C_{29}H_{48}N_2$ requires C, 82·0; H, 11·4; N, 6·6%).

Fucostenone.—α-Dihydrofucosterol (5 g.) in glacial acetic acid (150 c.c.) was treated first with bromine (2 g.) in acetic acid (50 c.c.) and then with a solution of chromic anhydride (1·5 g.) in acetic acid (50 c.c.; 90%), and the whole set aside for 15 hours. The solid separating after the addition of water was collected, washed with water, and debrominated by heating on a steam-bath for 10 minutes with zinc dust (20 g.) and glacial acetic acid (50 c.c.). The product, isolated by means of ether, separated from methyl alcohol in needles which after several recrystallisations from the same solvent had the constant m. p. 81—82°. α-Fucostenone separates with solvent of crystallisation which it holds tenaciously. *Light absorption in alcohol*: maxima, (a) 2405 A., log ε = 3·9; (b) 3150 A., log ε = 2·0. The *semicarbazone* separated from ethyl alcohol in needles, m. p. 250° (Found: C, 76·7; H, 10·5; N, 9·0. $C_{30}H_{51}ON_3$ requires C, 76·7; H, 10·9; N, 9·0%).

Fucostanyl Acetate.—The acetate described by Heilbron, Phipers, and Wright (*loc. cit.*; m. p. 127—129°, $[\alpha]_D^{20°}$ + 14·6°), after several recrystallisations from ethyl alcohol, had the constant m. p. 128—129—130° and $[\alpha]_D^{20°}$ + 15·1° (l = 1, c = 1·558 in chloroform).

Fucostanol.—Hydrolysis of this acetate with alcoholic potash, followed by repeated crystallisation of the product from methyl alcohol, gave fucostanol of constant m. p. 134·5—135—136°, which after prolonged desiccation had $[\alpha]_D^{20°}$ + 24·7° (l = 1, c = 1·336 in chloroform).

Fucostanyl 3 : 5-Dinitrobenzoate.—A solution of fucostanol ($[\alpha]_D^{20°}$ + 24·7°; 1 g.) in pyrid-

* This determination was made by Mr. R. N. Jones, to whom we express our thanks.

(6 c.c.) was heated on a steam-bath for 1 hour with 3 : 5-dinitrobenzoyl chloride (1 g.). The solution was poured into water, and the precipitated solid repeatedly crystallised from ethyl acetate, from which *fucostanyl* 3 : *5-dinitrobenzoate* separated in colourless plates of constant m. p. 214—215°, $[\alpha]_D^{20°}$ + 13·8° (l = 1, c = 1·447 in benzene) (Found: C, 70·7; H, 8·6; N, 4·8. $C_{36}H_{54}O_6N_2$ requires C, 70·8; H, 8·9; N, 4·6%).

Fucostanyl Benzoate.—Fucostanol ($[\alpha]_D^{20°}$ +24·7°; 1 g.) in pyridine (4 c.c.) was heated on the steam-bath for 30 minutes with benzoyl chloride (3 c.c.). Methyl alcohol (50 c.c.) was added, and the mixture refluxed for 5 minutes. The *benzoate* separated on cooling and after several crystallisations from ethyl acetate it formed plates of constant m. p. 135—136° (Found: C, 82·9; H, 11·1. $C_{36}H_{56}O_2$ requires C, 83·0; H, 10·8%).

Fucostanone.—Oxidation of fucostanol ($[\alpha]_D^{20°}$ + 24·7°) by the method described by Heilbron, Phipers, and Wright (*loc. cit.*), followed by separation of the neutral product and crystallisation of this from methyl alcohol, gave fucostanone in needles, m. p. 157°, $[\alpha]_D^{20°}$ + 40·2° (l = 1, c = 1·518 in chloroform). The oxime separated from methyl alcohol in needles, m. p. 217—218°, $[\alpha]_D^{20°}$ + 30·1° (l = 1, c = 1·356 in chloroform).

Fucostanedicarboxylic Acid.—The acidic *product* obtained from the oxidation described above, after several crystallisations from methyl alcohol, separated in colourless plates of constant m. p. 227—229° (Found: C, 75·4; H, 10·5. $C_{29}H_{50}O_4$ requires C, 75·3; H, 10·9). The *dimethyl* ester, prepared by means of diazomethane, separated from methyl alcohol in plates, m. p. 89—90° (Found: C, 75·8; H, 11·0. $C_{31}H_{54}O_4$ requires C, 75·85; H, 11·1%).

Epifucostanol.—A solution of fucostanone (6 g.) in acetic acid (150 c.c.; 96%) and hydrogen bromide (2 c.c.; 48%) was shaken at 60° with hydrogen in the presence of reduced platinum oxide (0·5 g.) for 3 hours. The solid precipitated from the filtered solution with water was collected and directly hydrolysed by refluxing for 2 hours with methyl-alcoholic potash (300 c.c.; 10%). The product was crystallised from methyl alcohol, from which *epifucostanol* separated in needles, m. p. 200°, $[\alpha]_D^{20°}$ + 25·5° (l = 1, c = 1·80 in chloroform) (Found: C, 83·3; H, 12·0. $C_{29}H_{50}O$ requires C, 83·5; H, 12·4%). The *acetate* separated from methyl alcohol in plates, m. p. 86—87°, $[\alpha]_D^{20°}$ + 27·4° (l = 1, c = 1·79 in chloroform) (Found: C, 81·1; H, 12·0. $C_{31}H_{54}O_2$ requires C, 81·1; H, 11·9%).

We desire to express our thanks to Imperial Chemical Industries Limited for a grant.

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168. *The Caryophyllenes. Part IV.*

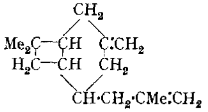
By G. R. RAMAGE and J. L. SIMONSEN.

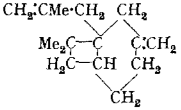
In Part I (J., 1934, 1806), where the isolation of caryophyllenic and norcaryophyllenic acids was first described, the assumption was made that these acids had the *cis*-configuration. This appeared to be justified (a) by the fact that norcaryophyllenic acid gave on digestion with acetyl chloride an oil only slowly soluble in sodium carbonate solution and (b) by analogy with pinic and norpinic acids. In view of synthetical experiments now in progress, it became necessary to confirm this configuration, more especially since it has been shown by Rydon (this vol., p. 593) and by Ruzicka, Zimmermann, and Huber (*Helv. Chim. Acta*, 1936, **19**, 343) that norcaryophyllenic acid, m. p. 126°, is the *trans*-acid, the *cis*-acid having m. p. 149—150°. Since we had been able to degrade caryophyllenic acid to norcaryophyllenic acid, m. p. 126° (J., 1935, 532), it appeared to us probable that the former acid also had the *trans*-configuration. This we have now been able to confirm. When *trans-d*-caryophyllenic acid, m. p. 80—81°, is heated with acetic anhydride at 220° under pressure, it yields the liquid *anhydride*, b. p. 157—158°/12 mm., of the *cis*-acid, from which the acid can be obtained by digestion with water. cis-*Caryophyllenic acid*, which is feebly lævorotatory, has m. p. 77—78°, and thus differs little in melting point from the *trans*-acid, although a mixture of the two begins to soften at about 65°. They can, however, readily be distinguished by the preparation of the *dianilides*, that derived from the *trans*-acid being very sparingly soluble.

In our last communication (J., 1935, 1581) we drew attention to the important bearing which the keto-acid, $C_{11}H_{18}O_3$, first prepared by Semmler and Mayer (*Ber.*, 1911, **44**, 3662)

had on the structure of β- and γ-caryophyllenes. It was stated by these authors that this acid behaved abnormally with sodium hypobromite, being oxidised, not to homocaryophyllenic acid, $C_{10}H_{16}O_4$, but to caryophyllenic and *as*-dimethylsuccinic acids. We have now repeated this oxidation with a pure specimen of the keto-acid regenerated from the semicarbazone and in agreement with Ruzicka and Wind (*Helv. Chim. Acta*, **1931**, **14**, 422) find the oxidation to proceed normally. Homocaryophyllenic acid, which is an oil, has been characterised by the preparation of the *dianilide*, m. p. 179—180°. This acid has become of increased interest, since Treibs (*Ber.*, 1936, **69**, 41) considers it to be formed also by the degradation of betulol.

We suggested (*loc. cit.*, p. 1582) that β- and γ-caryophyllenes differed in that the former contained an *iso*propenyl and the latter an *iso*propylidene group in the side chain. On this assumption it was anticipated that oxidation of γ-caryophyllene nitrosochloride would provide a convenient route to the above-mentioned keto-acid. Preliminary experiments, made in collaboration with Mr. W. G. Wainwright, B.Sc., have shown the main products of the ozonolysis to be neutral and they lead us to suggest that γ-caryophyllene may possibly be more correctly represented by either (I) or (II). If this should prove to be correct,

(I.) 

 (II.)

the keto-acid must originate from the " tautomeric " *iso*propylidene form of β-caryophyllene. It is hoped that experiments now in progress may enable us to elucidate this point.

Experimental.

cis-*Caryophyllenic Acid*.—*trans*-*d*-Caryophyllenic acid (10 g.) was heated with acetic anhydride (25 c.c.) at 220° for 6 hours; fractionation of the oil gave *caryophyllenic anhydride* (6 g.), b. p. 157—158°/12 mm. (Found : C, 64·6; H, 7·1. $C_9H_{12}O_3$ requires C, 64·3; H, 7·1%). After the anhydride had been boiled with water, slow evaporation of the solvent gave cis-*caryophyllenic acid*, m. p. 77—78°, in large glassy prisms; in chloroform (*c*, 3·645) $[\alpha]_{5461}$ − 7·4° (Found : C, 57·9; H, 7·4. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%). The acid was more readily soluble in the ordinary organic solvents than the *trans*-acid and it crystallised from *cyclo*hexane in long needles, m. p. 78°. In admixture with the *trans*-acid, softening occurred at 65°, but the mixture did not clear until 85—87°, well above the m. p.'s of the two constituents. Like the *trans*-acid, the *cis*-acid gave a sparingly soluble copper salt with copper acetate. The *dianilide* crystallised from dilute alcohol (50%) in long fine needles, m. p. 190° (Found : N, 8·2. $C_{21}H_{24}O_2N_2$ requires N, 8·3%). The *dianilide* of the *trans*-acid separated from *cyclo*hexanone in plates, m. p. 282°, very sparingly soluble in alcohol and acetone (Found : N, 8·4%). The *di*-p-*phenylphenacyl* ester of the *trans*-acid crystallised from alcohol in balls of needles, m. p. 121—122°, with softening at 117° (Found : C, 77·8; H, 6·1. $C_{37}H_{34}O_6$ requires C, 77·4; H, 5·9%).

Homocaryophyllenic Acid.—The semicarbazone of the keto-acid (2·5 g.) was hydrolysed by heating on the water-bath with dilute sulphuric acid (10%) for 30 minutes. The keto-acid was extracted in ether, converted into the sodium salt, and treated ice-cold with an excess of sodium hypobromite for 1 hour; the bromoform was then removed by ether. Homocaryophyllenic acid was isolated, after acidification of the alkaline solution, as an oil (2 g.) (Found : *M*, 198. Calc. : *M*, 200). The *dianilide* was obtained solid by the slow evaporation of its solution in dilute acetone; it then crystallised from dilute alcohol (50%) in plates, m. p. 179—180° (Found : C, 75·0; H, 7·5; N, 8·0. $C_{22}H_{26}O_2N_2$ requires C, 75·4; H, 7·4; N, 8·0%). The diamide and the di-*p*-phenylphenacyl ester were prepared but could not be obtained crystalline.

We are indebted to the Government Grants Committee of the Royal Society, to the Chemical Society, and to Imperial Chemical Industries, Ltd., for grants.

University College of North Wales, Bangor. [*Received, April 9th, 1938.*]

169. *Alkaloids of* Senecio. *Part II. Senecionine and Squalidine.*

By G. Barger and J. J. Blackie.

The first alkaloid of this genus was discovered long ago by Grandval and Lajoux (*J. Chim. Pharm.*, 1895, **2**, 15) in *S. vulgaris*, the common groundsel, and named senecionine. We have of late examined nearly every British species of *Senecio* and find that they mostly contain two or three very similar alkaloids which are sometimes difficult to separate, partly because of their scarcity. It seems essential that purification should be checked by optical activity, a point neglected by some previous workers; the melting point is no adequate criterion of purity. We are unable to confirm either Grandval and Lajoux's formula $C_{18}H_{25}O_6N$ or that of Manske, $C_{18}H_{23}O_5N$ (*Canadian J. Res.*, 1936, **14**, 8). In both investigations impure preparations seem to have been analysed (see experimental part). We ourselves remained in doubt as to the exact number of hydrogen atoms in senecionine as long as we worked with the summer alkaloids of that species. From *S. viscosus* and *S. squalidus* we, however, at once obtained pure senecionine of higher melting point and constant rotation, and found that in April and September the very small amount of alkaloid in *S. vulgaris* (0·02% or less) is also pure senecionine. In the summer it is temporarily accompanied by another base, but we have been unable to separate the mixture. Our pure senecionine gave accurate analyses for $C_{18}H_{25}O_5N$ and this formula is confirmed by those of the fission products formed according to the equation

$$C_{18}H_{25}O_5N + H_2O = C_8H_{13}O_2N + C_{10}H_{14}O_4$$

The basic fission product is, as Manske surmised, retronecine, first obtained from retrorsine of *S. retrorsus*. We find also an identical rotation. Manske did not succeed in purifying the acid for analysis, nor could we as long as we worked with impure senecionine, but later we were able to characterise it completely and suggest the name *senecic acid*. It is an unsaturated lactonic acid; it is reduced to *dihydrosenecic acid*, $C_{10}H_{16}O_4$, and must be acyclic. Retronecic acid, $C_{10}H_{16}O_6$, and a similar acid obtained from the alkaloids of South African species are saturated dihydroxydicarboxylic acids which must be monocyclic. The difference between these two kinds of acids is further shown by a determination of *C*-alkyl groups by Dr. H. Roth of Heidelberg, according to the oxidation method with chromic acid worked out by him. The results indicate that senecic acid furnishes three, but retronecic acid only two, equivalents of acetic acid, and we consider that retronecic acid has a five-membered ring, as has camphoric acid. The numerous acid fission products of the *Senecio* alkaloids, which vary much more than the basic moiety, are evidently examples of terpene acids, not hitherto observed in nature. Senecic acid on oxidation with nitric acid (presumably at the double bond) readily yields an acid $C_6H_8O_4$ in which the lactone group of senecic acid still survives. We are attempting to identify this acid.

Senecionine contains one reactive hydrogen atom present in the unesterified hydroxyl group of retronecine. In retrorsine the second hydroxyl is presumably in the acid moiety, the lactone acid corresponding to retronecic acid.

In *S. viscosus* we found no subsidiary alkaloid. In *S. vulgaris* one is present, which we could not separate, nor have we as yet obtained the very bitter ether-soluble senecine of Grandval and Lajoux, of which they only obtained a few milligrams and did not give any other properties. From *S. squalidus* we obtained a minute quantity of a new alkaloid, *squalidine*, isomeric with senecionine and having a lower melting point and great solubility in alcohol. Like senecionine, squalidine is an ester of retronecine, but the acid, squalinecic acid, is different, although, like senecic acid, it is unsaturated and therefore acyclic. We had not enough material to characterise it completely.

Experimental.

Senecionine from S. viscosus.—27 Kg. (dry) of this not very common species were collected in July, 1934, on a newly made embankment near Cockburnspath, mixed with 5% of calcium hydroxide, and percolated with 90% alcohol. After evaporation, the extract was mixed with dilute hydrochloric acid; the filtered acid solution was washed with ether, basified with ammonia,

and extracted with chloroform. After a second passage through acid, the second chloroform extract left a crystalline residue, which was recrystallised from alcohol; yield, 16·2 g. (0·06%). 370 G. collected early in the summer gave 0·28 g. (0·075%).

The alkaloid was pure senecionine and crystallised in rhomb-shaped plates, m. p. 232°, $[\alpha]_D$ − 54·6° and − 55·6° from two separate batches (*c* 1·63 and 4·60, respectively, in chloroform) (Found: C, 64·4; H, 7·5; N, 4·2. Calc. for $C_{18}H_{25}O_5N$: C, 64·5; H, 7·5; N, 4·2%).

Senecionine from S. vulgaris.—2·7 Kg. (dry) collected in April, 5·5 kg. collected in June, and 20 kg. collected in September gave 0·4 g. (0·015%), 3·3 g. (0·06%), and 3·1 g. (0·015%), respectively. The April and the September alkaloid had m. p. 232° and $[\alpha]_D$ − 55·6° (*c* 4·91, chloroform) and were therefore pure senecionine, but the higher content in June is accounted for, at least in part, by the appearance of another alkaloid which again disappears during the summer. The mixture of June alkaloids had m. p. 220°, $[\alpha]_D$ − 80·9°. The rotation is almost identical with that given by Grandval and Lajoux (− 80·5°), who seem to have had a similar mixture. Our material had a homogeneous appearance and did not change much on repeated crystallisation from alcohol, but the melting point remained low and the analyses were not sharp (Found: C, 63·8, 64·3, 64·4, 64·2; H, 7·3, 7·1, 7·1, 7·2; N, 4·1, 4·2. Calc. for $C_{18}H_{25}O_5N$: C, 64·5; H, 7·5; N, 4·2%. Calc. for $C_{18}H_{23}O_5N$: C, 64·9; H, 7·0; N, 4·2%). Grandval and Lajoux quote one analysis agreeing closely with the formula $C_{18}H_{25}O_6N$, which is certainly wrong. Manske's single analysis gives the carbon 1·8% low for his formula $C_{18}H_{23}O_5N$; his hydrogen (7·2%) is the mean quoted above for our mixture and his m. p. 222° is very similar. The alkaloid accompanying senecionine must have a higher lævorotation and probably less hydrogen than senecionine, but we were unable to isolate either it or pure senecionine from the mixture.

Senecionine from S. squalidus.—13·75 Kg. (dry) of this species, collected in July, 1935, from the station yard at Oxford (the only place in Britain where it is plentiful), yielded 8·2 g. (0·06%) of mixed alkaloids consisting almost entirely of senecionine, which was readily obtained pure, and 0·7 g. (0·005%) of a much more soluble new alkaloid, *squalidine*, having $[\alpha]_D$ − 26·9° (see below). After the first crystallisation the rotation of the senecionine was accordingly somewhat low (− 52·3° instead of − 55°).

Properties and Salts (m. p., rotation, analyses, see above).—Senecionine dissolves in *ca.* 340 parts of absolute alcohol at 15°, is hardly soluble in water and ether, but readily in chloroform. The solubility in water is so slight that it tastes less bitter than other *Senecio* alkaloids, but its salts are intensely bitter. It sublimes slowly at 130—140°/0·2 mm., rapidly at 190°, without decomposition. It has one hydroxyl group instead of two in retrorsine, which latter is accordingly more soluble in water and alcohol and less volatile. Active hydrogen (Zerewitinoff), 0·89, 0·90 equivalent. Senecionine readily decolorises alkaline permanganate (owing to a double bond in the acidic moiety). *Senecionine nitrate*, prepared by dissolving the base in the calculated quantity of 0·1*N*-acid and evaporating the solution, crystallises from water in prisms, and from absolute alcohol in rhombic plates, m. p. 214°, $[\alpha]_D$ − 34·2° (*c* 1·14 in water) (Found: C, 54·4; H, 6·5. $C_{18}H_{25}O_5N,HNO_3$ requires C, 54·3; H, 6·5%). The picrate forms fine needles, m. p. 191°, from dilute solution; the methiodide is sparingly soluble in absolute alcohol, much more soluble in 80% alcohol, and forms prisms, m. p. 249°; the aurichloride forms needles, m. p. 186°.

Hydrolysis.—This was effected as in the case of retrorsine, the plaster of Paris method described in Part I (J., 1935, 13) being used for the separation of the fission products. The base obtained was retronecine, $[\alpha]_D$ + 52·1° (*c* 2·5 in absolute alcohol) (from *S. viscosus*), + 52·2° (*c* 2·05) (from *S. vulgaris*); the m. p. in both cases and also of a mixture with retronecine from *S. retrorsus* was 118°. The purification of *senecic acid* was much more difficult. Although the acid crystallised on spontaneous evaporation of the ethereal extract of the plaster of Paris, it could not readily be recrystallised. By distillation at 180°/0·1 mm. we obtained a gum; its solution in chloroform was greatly concentrated, and addition of light petroleum then produced a semi-solid mass of aggregates of needles. This was filtered off, drained on porous plate, and washed with ether–petroleum (1 : 5) (light petroleum alone made it viscous); m. p. 147°. Ultimately, by spontaneous evaporation of the solution in *dry* ether we obtained needles, m. p. 153°, subliming without decomposition in a high vacuum, soluble in about 100 parts of cold water and crystallising from hot water in flat prisms, $[\alpha]_D$ + 41·8° (*c* 1·29 in absolute alcohol) (Found: C, 60·5, 60·6; H, 7·1, 7·2. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%). The equiv. by titration with 0·1*N*-sodium hydroxide in the cold was 198; at 100°, only slightly more alkali was neutralised; heated with a total of 3 mols. of 0·1*N*-sodium hydroxide at 100° for some minutes, the acid neutralised 2 proportions; hence equiv., 99. A lactone acid $C_{10}H_{14}O_4$ requires 198 and 99. The lactone group seems to be unusually stable, and is not readily re-formed,

for on heating with 3 equivs. of alkali, addition of 3 equivs. of hydrochloric acid, and keeping at room temperature for 10 days, the solution still neutralised 2 equivs. of alkali, so that both carboxyl groups were still free. After strong acidification with hydrochloric acid, and continuous extraction with ether, a small yield of the original lactone acid, m. p. 153°, was obtained.

Senecic acid reduced alkaline permanganate and apparently contains three *C*-alkyl groups (Found : acetic acid after oxidation with chromic acid, 2·90, 2·88 equivs.; Dr. H. Roth).

Dihydrosenecic Acid.—Senecic acid (99 mg.) in a mixture of methyl alcohol, water, and a little acetic acid, shaken with platinum oxide, took up about 1 equiv. of hydrogen in ½ hour. After filtration and evaporation, the product did not crystallise; it was therefore distilled (at 180°/0·2 mm.). The gummy distillate was dissolved in benzene; it crystallised, on scratching and gradual addition of 2 vols. of petroleum, in long slender needles (20 mg.), m. p. 106° (Found : C, 59·5; H, 8·2. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·1%).

Oxidation of Senecic Acid.—460 Mg. of the crude acid, repeatedly evaporated on the water-bath with concentrated nitric acid, yielded 107 mg. of an oxidation product, crystallising from water; recrystallised from ethyl acetate with petrol, a first fraction (30 mg.) was obtained, m. p. 142° (Found : C, 49·7; H, 5·2. Found after sublimation : C, 49·9; H, 5·5; equiv. in the cold, 144 ± 5. $C_6H_6O_4$ requires C, 50·0; H, 5·6%; equiv., 144). The *substance* contains apparently two *C*-alkyl groups (Found : 1·68, 1·69 equivs. of acetic acid; Dr. H. Roth). Synthetic αβ-dimethylmalic acid similarly yielded 1·90, 1·91 equivs. of acetic acid; the oxidation product of senecic acid does not appear to be its lactone.

Squalidine from S. squalidus.—A minute quantity (0·005% of the dry plant) remained in the mother-liquor from the crystallisation of senecionine. It is much more soluble in alcohol than the latter alkaloid and separates on concentration in crystals, of a very bitter taste, m. p. 169°, $[\alpha]_D^{16°}$ − 26·9° (*c* 1·45, chloroform) (Found : C, 64·3, 64·5; H, 7·9, 7·6; N, 4·4. $C_{18}H_{25}O_5N$ requires C, 64·5; H, 7·5; N, 4·2%). The alkaloid is therefore isomeric with senecionine. It is distinctly volatile in a high vacuum at 70°, over one-third being lost when the specimen was dried for analysis. The nitrate crystallised from absolute alcohol; m. p. 204°, $[\alpha]_D^{16°}$ − 8·65° (*c* 2·08 in water). The picrate formed needles, m. p. 203°, from dilute alcohol. On hydrolysis squalidine yielded a base, which was distilled in a high vacuum; m. p. 115°. The mixture with retronecine (m. p. 119°) melted at 115°; the base is almost certainly retronecine.

Squalinecic Acid.—The acid differs from senecic acid, to which it is, however, probably closely related. It was first obtained as a syrup, twice distilled in a high vacuum (bath at 130°), and crystallised by inoculation with senecic acid. Recrystallisation from benzene by addition of petroleum gave slender needles, m. p. 129°; it was, however, not pure (Found: C, 57·1; H, 7·2. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%. $C_{10}H_{16}O_5$ requires C, 55·6; H, 7·4%). Like senecic acid, squalinecic acid reduces alkaline permanganate and is therefore acyclic. Like senecic acid, it contains 3 *C*-alkyl groups (Found: 2·75, 2·77; calc. for $C_{10}H_{16}O_5$).

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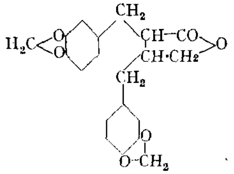
170. *The Constituents of Natural Phenolic Resins. Part VI. Synthesis of Compounds Related to Cubebinolide (Hinokinin).*

By ROBERT D. HAWORTH and WILLIAM KELLY.

ANALOGY with the experiments described in Part I (J., 1935, 633) suggested that cubebinolide (hinokinin) (I) (see Part I, *loc. cit.*, and Part V, this vol., p. 725, for references) would yield the lactones (II) and (III) when treated with lead tetra-acetate. The present communication describes the synthesis of (II) and (III), which were prepared for comparison purposes. The lactone (II) was obtained by applying the method described in Part III (J., 1935, 1576). Owing to the instability of the methylenedioxy-group in the presence of acidic condensing agents, the method described in Part II (J., 1935, 636) does not provide a satisfactory route to the lactone (III); this, however, has been synthesised by employing reactions similar to those described in Part IV (this vol., p. 348).

Recently Dr. T. Ishiguro kindly sent us a generous specimen of *l*-hinokinin, but we have

been unable to discover appropriate conditions for the conversion of either *l*- or *dl*-hinokinin (compare Part V, *loc. cit.*) into the lactones (II) and (III). In numerous experiments,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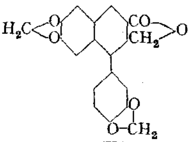
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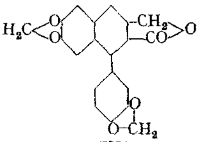
(III.)

either unchanged hinokinin or amorphous substances, probably catechol derivatives, which dissolved and rapidly darkened in warm dilute aqueous alkalis, were obtained. This attack of the methylenedioxy-group by lead tetra-acetate is not consistent with the stability of the group during the synthesis of dehydroanhydropicropodophyllin (Part IV, *loc. cit.*).

Experimental.

6 : 7-*Methylenedioxy*-1-(3′ : 4′-*methylenedioxyphenyl*)*naphthalene*-2 : 3-*dicarboxylic Acid*.—3 : 4-Methylenedioxyphenylpropiolic acid (2·8 g.), m. p. 165° (Baude and Reychler, *Bull. Soc. chim.*, 1897, **17**, 617) and acetic anhydride (18 c.c.) were heated at 100° for 4 hours. The *anhydride*, which separated on cooling, crystallised from glacial acetic acid in yellow prisms (2 g.), m. p. 244—246° (Found: C, 66·1; H, 2·9. $C_{20}H_{10}O_7$ requires C, 66·3; H, 2·8%). The *methyl* ester, prepared by heating the anhydride with methyl-alcoholic hydrogen chloride for 12 hours, crystallised from methyl alcohol–chloroform in colourless prisms, m. p. 214—215° (Found: C, 64·8; H, 4·2. $C_{22}H_{16}O_8$ requires C, 64·7; H, 3·9%).

Methylenedioxybenzene.—The following method, suggested by the work of Stevens (J., 1935, 725), proved most convenient. 4 : 5-Dibromo-1 : 2-methylenedioxybenzene (10 g.) (prepared from piperonylic acid by the method of Jones and Robinson, J., 1917, 913) was dissolved in 70% methyl alcohol (120 c.c.), and 4% sodium amalgam added. After boiling for 24 hours, most of the alcohol was removed through a good column, and the residue extracted with light petroleum (b. p. 40—60°). Yield, 3·5 g.; b. p. 172°.

β-(3 : 4-*Methylenedioxybenzoyl*)*propionic Acid*.—In spite of considerable demethylenation the following method is more convenient than Bougault's (*Ann. Chim.*, 1908, **15**, 515). Aluminium chloride (5·5 g.) in nitrobenzene (30 c.c.) was gradually added to an ice-cold mixture of methylenedioxybenzene (2 g.) and succinic anhydride (2 g.) in nitrobenzene (10 c.c.). After standing for 6 hours at room temperature, the mixture was cautiously acidified, the nitrobenzene removed in steam, and the hot residue filtered; on cooling, the filtrate deposited the crude acid (1 g.), which was obtained in colourless prisms (0·5 g.), m. p. 136° after three crystallisations from hot water (Bougault, *loc. cit.*, gives m. p. 136°).

β-(3 : 4-*Methylenedioxybenzoyl*)-α-(3′ : 4′-*methylenedioxybenzylidene*)*propionic Acid*.—The dry powdered sodium salt of the above acid (1·2 g.), piperonal (1·2 g.), and acetic anhydride (2 c.c.) were heated at 100° for 2 hours. Water was added, and the *γ-lactone* collected, washed successively with water, methyl alcohol and ether, and crystallised from acetic acid (carbon); small greenish-yellow needles (1·2 g.), m. p. 236—237°, were obtained (Found: C, 67·6; H, 3·8. $C_{19}H_{12}O_6$ requires C, 67·7; H, 3·6%). The γ-lactone (1·2 g.) was boiled for 1 hour with sodium ethoxide solution prepared from sodium (0·9 g.) and alcohol (7 c.c.). Water was added and the alcohol removed; the *acid*, precipitated by hydrochloric acid, crystallised from methyl alcohol in small colourless needles (0·7 g.), m. p. 193° (Found: C, 64·8; H, 4·1. $C_{19}H_{14}O_7$ requires C, 64·4; H, 4·0%).

β-(3 : 4-*Methylenedioxybenzoyl*)-α-(3′ : 4′-*methylenedioxybenzylidene*)-β-*methylenepropionic Acid*.—A mixture of the above acid (0·4 g.), 10% sodium hydroxide solution (2 c.c.), and 20% formalin (1 c.c.) was allowed to react for 12 hours. After addition of dilute sulphuric acid the *product* was isolated with chloroform; it crystallised from benzene in small colourless nodules (0·3 g.), m. p. 184—185° (Found: C, 65·4; H, 3·7. $C_{20}H_{14}O_7$ requires C, 65·6; H, 3·8%).

Lactone of 6 : 7-*Methylenedioxy*-1-(3′ : 4′-*methylenedioxyphenyl*)-2-*hydroxymethylnaphthalene*-3-*carboxylic Acid* (II).—A mixture of the above methylene acid (0·5 g.), glacial acetic acid (9 c.c.),

and concentrated hydrochloric acid (10 c.c.) was kept for 12 hours. After addition of water, the product was collected, heated at 100° with 5% sodium hydroxide solution (5 c.c.) for 15 minutes, and filtered off. The filtrate was acidified and heated at 100° for 1 hour and the product, after digestion with sodium bicarbonate solution for ½ hour, was collected and crystallised from methyl alcohol–chloroform (carbon); colourless prisms (0·3 g.), m. p. 264°, were obtained (Found: C, 68·8; H, 3·5. $C_{20}H_{12}O_6$ requires C, 69·0; H, 3·5%). This *lactone* can also be purified by sublimation at 0·5 mm. The lactone (II) was converted into 6 : 7-methylenedioxy-1-(3′ : 4′-methylenedioxyphenyl)naphthalene-2 : 3-dicarboxylic acid by oxidation with potassium permanganate under conditions similar to those employed for the corresponding tetramethoxy-lactone (Part II, *loc. cit.*, p. 643).

Bis-(3 : 4-*methylenedioxyphenyl*)*methylsuccinic Acid*.—A mixture of glacial acetic acid (8 c.c.) and concentrated sulphuric acid (8 c.c.) was gradually added to an ice-cold solution of methylenedioxybenzene (2·4 g.) and ethyl hydroxymethylenesuccinate (2 g.) in acetic acid (8 c.c.). After 12 hours, ice was added and the product, isolated with chloroform, was hydrolysed by warming with 10% methyl-alcoholic potassium hydroxide (10 c.c.) for 2 hours. Unchanged methylenedioxybenzene was removed in steam and acidification of the residue yielded the *acid*, which crystallised from 20% acetic acid (carbon) in colourless prisms (0·6 g.), m. p. 140° with previous shrinking from 130° (Found: C, 58·6; H, 4·6; equiv., 183. $C_{19}H_{16}O_8,H_2O$ requires C, 58·5; H, 4·6; equiv., 186). Attempts to convert this acid into the corresponding 4-ketotetrahydronaphthalene derivative were unsuccessful.

α-(3 : 4-*Methylenedioxybenzoyl*)-β-(3 : 4-*methylenedioxybenzyl*)*butyrolactone*.—The sodio-derivative prepared from α-acetyl-β-(3 : 4-methylenedioxybenzyl)butyrolactone (5 g.) (Part IV, *loc. cit.*, p. 357) and sodium (0·45 g.) in benzene (10 c.c.), and 3 : 4-methylenedioxybenzoyl chloride (5·2 g.) in benzene (10 c.c.) were kept for 12 hours and then heated at 100° for 1 hour. The mixture was decomposed with water and washed with 2% sodium hydroxide solution, the benzene layer dried, and most of the solvent removed. The residue was dissolved in ether and shaken for 7 hours with 5% sodium hydroxide solution (120 c.c.). Water was added to dissolve the sodium salt which had separated and the alkaline liquor was separated, acidified, and extracted with chloroform. The extract was washed with sodium bicarbonate solution, the solvent removed, and the residue triturated with alcohol. The *lactone* crystallised from benzene in colourless prisms (2 g.), m. p. 136—137° (Found: C, 65·4; H, 4·4. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3%). A violet colour gradually developed when ferric chloride was added to an alcoholic solution of the lactone.

Lactone of 6 : 7-*Methylenedioxy*-1-(3′ : 4′-*methylenedioxyphenyl*)-3-*hydroxymethyl*-3 : 4-*dihydronaphthalene*-2-*carboxylic Acid*.—The above butyrolactone (1 g.) was warmed with methyl-alcoholic hydrogen chloride (15 c.c.) for 15 minutes; the product isolated with ether was an oil (0·9 g.), which was heated in a carbon dioxide stream in an oil-bath with potassium hydrogen sulphate (1·8 g.) at 155° for 6 hours. The *dihydro-lactone*, isolated with chloroform, was purified by repeated crystallisation from alcohol–chloroform; colourless prisms (0·1 g.), m. p. 228—229°, were obtained (Found: C, 68·3; H, 4·3. $C_{20}H_{14}O_6$ requires C, 68·6; H, 4·0%).

Lactone of 6 : 7-*Methylenedioxy*-1-(3′ : 4′-*methylenedioxyphenyl*)-3-*hydroxymethylnaphthalene*-2-*carboxylic Acid* (III).—The above dihydro-lactone (0·1 g.) and palladium-black (0·01 g.) were heated for ½ hour at 220°, and the mixture sublimed at 220°/0·2 mm. The *sublimate*, twice crystallised from alcohol–chloroform and finally from glacial acetic acid, was obtained in small slender prisms, m. p. 273—275° (Found: C, 69·0; H, 3·8. $C_{20}H_{12}O_6$ requires C, 69·0; H, 3·5%).

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171. *Experiments on the Synthesis of Substances Related to the Sterols. Part IX.*

By ROBERT ROBINSON and JAMES WALKER.

IN a recent communication (this vol., p. 50) Hewett stated that Robinson and Schlittler (J., 1935, 1288) "accepted" a view expressed by Cook and Hewett (J., 1933, 1105) to the effect that certain difficulties in the use of 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrenes for the synthesis of the sterol type of ring system could probably be overcome by the use of analogous derivatives of *as.*-octahydrophenanthrene.

The work of Robinson and Schlittler was greatly delayed in publication and our plans were in no way influenced by the comments of Cook and Hewett on their experiences. Furthermore the idea that oestrone, a derivative of octahydrophenanthrene, might be synthesised from simpler derivatives of the same polycyclic hydrocarbon does not appear to us to be particularly original and we "accepted" this view long ago in a more general form.

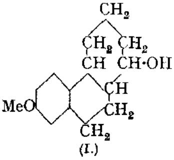
Hewett (*loc. cit.*) also comments on the fact that the method of Robinson and Schlittler for the synthesis of β-*m*-methoxyphenylethyl*cyclo*hexane-2 : 6-dione is lengthy. Unfortunately this is the case, but the process is the only known satisfactory method of preparation and we have now effected improvements at various stages (see Experimental). The ring closure of the dione to a phenanthrene derivative is a simple operation and can be brought about in various ways; we have retained the original method,* which is convenient and gives a yield exceeding 90%. In the hope of improving the preparation of 5-keto-8-*m*-methoxyphenyloctoic acid we have studied the formation of Grignard reagents from γ-*m*-methoxyphenylpropyl iodide and chloride. The organo-magnesium derivatives were readily produced and, after reaction with methyl chloroformate and hydrolysis of the product, γ-*m*-methoxyphenylbutyric acid was isolated. Interaction of γ-*m*-methoxyphenylpropylmagnesium chloride and β-chloropropionyl chloride afforded a mixture of products, including one that gave analytical data agreeing with the composition $C_{13}H_{17}O_2Cl$. The substance would appear to be the expected β-*chloroethyl* γ-m-*methoxyphenylpropyl ketone*, bnt its boiling point is abnormally high and in order to resolve the dubiety the investigation is being continued and extended to the zinc compounds.

Some further stages in one of the attempted syntheses of oestrone have now been realised and the first stereochemical hnrdle has been safely negotiated.

The reduction of 1-keto-7-methoxyhexahydrophenanthrene (Robinson and Schlittler, *loc. cit.*) to a ketomethoxyoctahydrophenanthrene could not be directly accomplished, although many conditions were tried. This contrasts with the practicability of the catalytic reduction of α-octalone to α-decalone (Hückel and Blohm, *Annalen*, 1933, **502**, 136) and of 2-keto-4-phenyl-$\Delta^{1:9}$-octalin to 2-keto-4-phenyldecalin (Rapson and Robinson, *J.*, 1935, 1286).

The product of the catalytic reduction of the ketomethoxyhexahydrophenanthrene was a solid *methoxyoctahydrophenanthrol*-a (I), apparently stereoisomeric (different *p*-nitrobenzoate) with that obtained by reduction of the unsaturated ketone with sodium and alcohol (Robinson and Schlittler, *loc. cit.*). The isomeride (a) is probably a derivative of *cis*-decalin, because it is almost homogeneous and yet gives a mixture of labile and stable ketones on oxidation. The diagnosis of these substances is not conclusive, but the indication is that the labile ketone includes rings fused in the *cis*-position.

The first attempt to oxidise the alcohol (I) was made with Beckmann's mixture and a naphthalene derivative was produced. This substance has been previously obtained by Butenandt and Schramm (*Ber.*, 1935, **68**, 2083), but no derivatives were described; it has also been mentioned without details by Cohen, Cook, and Hewett (this vol., p. 52).



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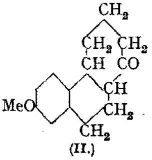
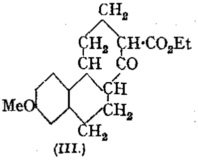


(II.)



(III.)

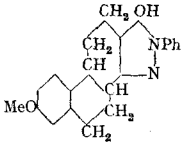
Under milder conditions of oxidation, chromic acid in an acetic acid medium effected partial conversion of (I) into the related ketone (II), but tbe yield was not very satisfactory.

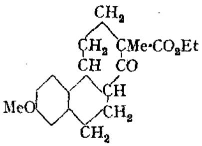
* The use of 80% sulphuric acid, as recommended by Hewett (*loc. cit.*), is also feasible but not a great improvement. We are familiar with the application of this reagent to such cyclisations: subject to correction and within our knowledge it was first used by Perkin, Rây, and Robinson (*J.*, 1927, 2097) for the dehydration of β-*m*-methoxyphenoxypropionic acid with formation of methoxychromanone.

The ketone was isolated in the form of its semicarbazone or by means of Girard's reagent and was eventually crystallised but only in part. The oily ketone afforded further crystals only after isomerisation under the influence of hot aqueous oxalic acid.

The crystallised ketone was homogeneous and *X*-ray crystallographic analysis, kindly carried out by Miss D. M. Crowfoot, made it very probable that it was the *trans*-modification. This is in harmony with the evidence for isomerisation of a more labile ketone and the conclusion is important because the stereochemical configuration of (II) is evidently that which is characteristic of oestrone in respect of the fusion of the *cyclo*hexane rings.

The *trans*-ketone (II) was condensed with ethyl oxalate in the presence of sodium ethoxide; the resulting diketo-ester decomposed, on heating, with formation of the β-keto-ester (III). This substance was characterised by conversion into a *phenylpyrazolone*

(IV.) 

 (V.)

(or *hydroxypyrazole*) (IV). Methylation of the ester (III) afforded (V), which gives no ferric reaction. The expression (V) applies to four optically inactive stereoisomeric forms, of which two could be obtained from the *trans*-ketone (II), and the next phase of this section of our work must be concerned with the isolation of one or both of the stereoisomerides.

Experimental.

Grignard Reagents from γ-m-*Methoxyphenylpropyl Iodide and Chloride.*—(A) γ-*m*-Methoxyphenylpropyl iodide (10·4 g.) was brought into reaction with magnesium (1·0 g.) in anhydrous ether (60 c.c.) and the mixture was eventually gently refluxed on the steam-bath until most of the metal had disappeared. An excess of methyl chloroformate was then introduced and, after the vigorous reaction had subsided, the product was worked up in the known manner. The γ-*m*-methoxyphenylbutyric ester produced was hydrolysed by means of aqueous methyl-alcoholic potassium hydroxide and the resulting γ-*m*-methoxyphenylbutyric acid was isolated (3·5 g.), m. p. 49—50° (Found: C, 68·1; H, 7·2. Calc. for $C_{11}H_{14}O_3$: C, 68·0; H, 7·2%). In a similar experiment with the chloride the yield was definitely improved, but a part of the product was lost.

(B) The reagent was prepared from magnesium (3·0 g.) and γ-*m*-methoxyphenylpropyl chloride (21 g.) in ether (100 c.c.), the mixture being finally refluxed for 3 hours. It was then cooled and added with vigorous stirring to a solution of β-chloropropionyl chloride (20 g.) in ether (50 c.c.). Under these conditions we thought it possible that a chloroethyl ketone might be formed and this substance would doubtless be convertible into (V) or the related alcohol by successive condensation with ethyl sodiomethylmalonate, two cyclisations, and reduction. After the usual treatment the following fractions were obtained: (a) 5·8 g. of a colourless mobile oil, b. p. up to 130°/0·2 mm., darkening on keeping; (b) 2·1 g. of a colourless oil, b.p. 130—180°/0·35 mm.; (c) 6·7 g. of a somewhat viscous oil, b. p. above 180°/0·35 mm. and mainly above 205°/0·27 mm. On redistillation, (c) gave 1·62 g., b. p. up to 195°/0·27 mm., $n_D^{14·5°}$ 1·5290; 2·3 g., b. p. 200—212°/0·27 mm., a colourless viscid oil, $n_D^{14·5°}$ 1·5456 (Found: C, 65·0; H, 7·1; Cl, 14·4. $C_{13}H_{17}O_2Cl$ requires C, 64·9; H, 7·1; Cl, 14·8%); and finally a fraction, b. p. 212—240°/0·27 mm., a viscous oil, $n_D^{14·5°}$ 1·5602. The analysis cited confirms an earlier estimation and it is difficult to explain the results on any basis other than the assumption that this fraction consists essentially of the expected β-*chloroethyl* γ-m-*methoxyphenylpropyl ketone.*

Methyl δ-*Keto*-8-m-*methoxyphenyloctoate.*—γ-*m*-Methoxyphenylbutyryl chloride and ethyl sodio-α-acetylglutarate were condensed in benzene solution, and the product treated in the earlier stages by the method previously described (*loc. cit.*). The mixture of methyl esters ultimately obtained was, however, completely separated (cf. this vol., p. 193) by one fractionation into methyl γ-*m*-methoxyphenylbutyrate, distilling up to 165°/0·3 mm., and, with no intermediate fraction, *methyl* δ-*keto*-8-m-*methoxyphenyloctoate*, distilling without residue at 180—187°/0·2 mm.

as a limpid, nearly colourless, viscous oil, $n_D^{16^\circ}$ 1·5095 (Found: C, 68·9; H, 8·0. $C_{16}H_{22}O_4$ requires C, 69·1; H, 7·9%).

From 242 g. of γ-*m*-methoxyphenylbutyric acid (treated in lots of 33 g.), there were obtained 154·2 g. (60%) of methyl γ-*m*-methoxyphenylbutyrate and 86·5 g. (25%) of methyl 5-keto-8-*m*-methoxyphenyloctoate.

β-m-*Methoxyphenylethyl*cyclo*hexane*-2 : 6-*dione*.—Methyl 5-keto-8-*m*-methoxyphenyloctoate (32·8 g.) was treated with alcohol-free sodium ethoxide (*J.*, 1935, 1290), and ice-water added to the reaction mixture. The strongly alkaline aqueous layer was extracted twice with ether and acidified with dilute sulphuric acid; the precipitated dihydroresorcinol compound (25·1 g.; 87%), after being washed with water and ether and dried in a vacuum, had m. p. 150°, and was evidently pure as first isolated. The dihydroresorcinol derivative (25 g.) when treated as described previously afforded 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene (21·1 g.) in 91% yield.

7-*Methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthr*-1-*ol*-a (I).—(A) The last-named ketone (19·1 g.) in methyl alcohol (230 c.c.) was shaken with a 2% palladised strontium carbonate catalyst (15 g.) in hydrogen under 2—3 atmospheres excess pressure. Absorption of the gas was regular and contiuuous and ceased when slightly less than 2 mols. had been absorbed in about 9 hours. The filtered solution was evaporated; the vitreous residue (19 g.) distilled at 164—169°/0·2 mm. as an extremely viscous syrup, which set to a colourless stiff glass when cold. Rubbing with methyl alcohol induced crystallisation and from this solvent the compound separated as a powder, which softened at 99—104° and cleared at 105° This m. p. was unaltered on further separation from methyl alcohol (Found: C, 77·5; H, 8·3. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%). The *compound* separated from ethyl acetate as a microcrystalline powder, which sintered at 106°, softened from 108°, and cleared at 111°.

(B) The ketone (1·2 g.) in pure ether (30 c.c.) was shaken in hydrogen under a slight pressure with colloidal palladium (0·1 g. of palladium chloride, 0·2 g. of gum arabic, and 90 c.c. of water). Steady absorption of hydrogen occurred, slightly more than 2 mols. being absorbed in a few hours. The product isolated (1·1 g.) did not react with Brady's reagent and it crystallised readily on nucleation with the tetrahydro-compound obtained as in (A).

The p-*nitrobenzoate* was obtained by the action of a slight excess of *p*-nitrobenzoyl chloride on the compound (40 mg.) in dry pyridine (0·5 c.c.) at room temperature. After 12 hours the mixture was treated with water and the *ester* was extracted in ether–ethyl acetate, the extract being washed with zinc chloride solution and dilute sodium carbonate solution. The ester separated from ethyl alcohol as a very pale yellow, micro-crystalliue powder, m. p. 125—126° after sintering at 120° (Found: C, 69·2; H, 6·2; N, 4·0. $C_{22}H_{23}O_5N$ requires C, 69·3; H, 6·0; N, 3·7%).

2 : 4-*Dinitrophenylhydrazone of* 1-*Keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—The above methoxyoctahydrophenanthrol (1·1 g.) was treated with Beckmann's mixture (30 c.c.) with shaking and warming on the steam-bath for about 45 minutes. The product was extracted with ether and the extract was washed with dilute sodium carbonate solution, dried, and evaporated. The crude product (0·75 g.) was distilled at 0·2 mm.; the distillate (*ca.* 0·4 g.) gave an immediate precipitate with Brady's reagent in warm alcoholic solution. The *hydrazone* was very sparingly soluble in the usual solvents and crystallised from pyridine in bright red needles, m. p. 304° (decomp.) (Found: C, 62·1; H, 4·5. $C_{21}H_{18}O_5N_4$ requires C, 62·1; H, 4·4%).

1-*Keto*-7-*methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (II).—(A) The above methoxyoctahydrophenanthrol (14 g.) in glacial acetic acid (70 c.c.) was mixed with a concentrated solution of chromic acid (4·5 g.; slight excess) in water. The solution was warmed to *ca.* 60° on the water-bath at intervals during 1¼ hours, kept for 12 hours at room temperature, and again warmed at 60° for ½ hour. The reaction mixture was added to ether and water (*ca.* 300 c.c.) and the ethereal solution was separated, washed with sodium bicarbonate solution, dried, and evaporated. The crude reddish-brown oil (13·6 g.) was treated at room temperature in alcoholic solution (40 c.c.) with a concentrated aqueous solution of semicarbazide hydrochloride (7 g.) and sodium acetate (9 g.) and the *semicarbazone* (6·6 g.) which separated in the course of a few hours was collected and dried in a vacuum. It was very sparingly soluble in methyl and ethyl alcohols and separated from a large volume of butyl alcohol in small, stout, colourless prisms, m. p. 225° (decomp.) (Found: C, 67·1, 67·2; H, 7·1, 7·4. $C_{16}H_{21}O_2N_3$ requires C, 66·9; H, 7·3%).

When refluxed for an hour with 20% aqueous oxalic acid, the semicarbazone was quantitatively hydrolysed. The ketone was extracted with ether and the extract, washed with dilute sodium carbonate solution, dried, and evaporated, yielded a semi-solid product: crystallisation

from methyl alcohol, or light petroleum, afforded colourless needles, m. p. 109° (Found: C, 78·3; H, 7·8. $C_{15}H_{18}O_2$ requires C, 78·3; H, 7·8%).

The 2 : 4-*dinitrophenylhydrazone* separated immediately as an orange precipitate when a warm solution of the ketone (34 mg.) in ethyl alcohol (0·5 c.c.) was mixed with a similar solution of 2 : 4-dinitrophenylhydrazine (30 mg.) containing a trace of concentrated sulphuric acid. The compound separated from ethyl acetate, containing a few drops of light petroleum, in small orange prisms, m. p. 209·5° (decomp.) after sintering at 205° (Found: C, 61·4; H, 5·3. $C_{21}H_{22}O_5N_4$ requires C, 61·5; H, 5·4%).

(B) The methoxyoctahydrophenanthrol (12·5 g.) in glacial acetic acid (60 c.c.) was oxidised during 1 hour on the steam-bath with chromic acid (4·0 g.; 10% excess) in 75% acetic acid (20 c.c.). The reaction mixture was treated as before and the crude product was dissolved in 65% ethyl alcohol (60 c.c.) and boiled under reflux for 1·5 hours with Girard's pyridine betaine-hydrazide reagent (*Chem. Zentr.*, 1935, I, 959) (12 g.). The alcoholic solution was cooled, mixed with ether, and added to water (*ca.* 250 c.c.). The aqueous solution was rapidly separated, washed with ether, mixed with concentrated hydrochloric acid (90 c.c.), and warmed on the water-bath for ½ hour. The ethereal solution furnished 7·43 g. of unchanged alcohol after drying, evaporation, and vacuum distillation. The ketone was isolated from the hydrolysis by means of ether, and the crude product (5·0 g.) on distillation in a vacuum furnished a colourless viscous oil (4·3 g.), b. p. 165—173°/0·23 mm. On crystallisation from methyl alcohol, only a part (1·35 g.) of this material separated in the crystalline form and the mother-liquor furnished a non-crystallising oil. The oil was refluxed with 20% oxalic acid solution for an hour and isolated as before; crystallisation from methyl alcohol then furnished a further quantity (1·1 g.) of crystalline material. The oil (1·8 g.) from the second mother-liquor was submitted again to treatment with oxalic acid, yielding still more crystalline material (0·6 g.). The residual oil finally obtained probably contained a small amount of the dehydro-ketone (see above), as was indicated qualitatively by the red colour of the precipitate obtained with Brady's reagent.

Crystallisation from light petroleum gave crystals better suited for *X*-ray analysis than those separating from methyl alcohol and we are grateful to Miss D. M. Crowfoot for the following report:

The crystals were in the form of needles elongated along *b* and flattened on (100). Optically they were positive, α along *b*, γ about 5° from *c* in the obtuse angle. Optic axial angle large, double refraction high. There is a marked *b* cleavage.

The *X*-ray measurements gave: $a = 12·0$; $b = 8·1$; $c = 12·9$ A.; $\beta = 105°$; $n = 4$ for $\rho = 1·245$; $h0l$ absent for $h + l$ odd, also apparently $0kl$ for k odd; $0k0$ absent for k odd; space group, $P2_1/n$.

This space group indicates that there are present two enantiomorphic molecules related by the *n* glide plane. Following the optics, the arrangement of the molecules is most probably with the length closely along *c* (γ), the width in *a* (β) and thickness in *b* (α).

(020) is, however, not nearly so powerful a reflection as (120) and there is therefore most probably slanting of the molecules across this plane. This requires fairly close packing all round, and while it is just possible to fit a *cis*-form into the cell, it appears much more probable that it is the *trans*-form which is present.

Ethyl 1-*Keto*-7-*methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-2-*carboxylate* (III).—Methoxyoctahydrophenanthrone (4·0 g.) and ethyl oxalate (2·65 g.) were mixed with pure dry ether (65 c.c.), a small amount of the ketone remaining in suspension. Freshly prepared alcohol-free sodium ethoxide (1·44 g.) was added to the mixture in lumps, which were disintegrated by means of a glass rod. The sodium ethoxide rapidly dissolved with slight evolution of heat and soon afterwards the separation of an orange sodio-derivative commenced. After 2 days at room temperature, ice-water and dilute sulphuric acid were added and the ethereal solution was rapidly separated, dried, and concentrated; the orange-brown syrup obtained gave a blood-red colour with alcoholic ferric chloride. The crude product was heated at 180—190° for 3 hours, a fairly brisk effervescence taking place during the first hour. On distillation in a vacuum, unchanged ketone was not recovered and a yellow viscous syrup (3·41 g.) distilled at 195—205°/0·35 mm., $n_D^{16°}$ 1·5645. The product gave with alcoholic ferric chloride a violet colour, changing to brown on the addition of ether. It was characterised as the related phenyl-pyrazolone derivative.

The keto-ester (0·29 g.) was mixed with phenylhydrazine (0·16 g.) and heated on a boiling water-bath for 3 hours. The yellow solid obtained was cooled, triturated with ether, collected, and washed with much ether, giving a colourless powder (0·18 g.) very sparingly soluble in the usual solvents. The substance separated from 60% aqueous pyridine in clusters of colourless

microscopic, thin, trapezoidal plates, m. p. 258—260° (decomp.) after sintering at about 230° and slight softening from 245° (Found: C, 76·5; H, 6·3; N, 8·3. $C_{32}H_{32}O_2N_2$ requires C, 76·3; H, 6·3; N, 8·1%). It is evidently the expected 5-*hydroxy*-1-*phenyl*-3 : 4-(7′-*methoxy*-3′ : 4′ : 9′ : 10′ : 11′ : 12′-*hexahydrophenanthreno*-1′ : 2′)*pyrazole* (IV).

Ethyl 1-*Keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-2-*carboxylate* (V).—The above keto-ester (4·9 g.) in dry benzene (25 c.c.) was added to powdered potassium (0·7 g.; 10% excess) in benzene (25 c.c.). The potassium rapidly dissolved, giving a dark amber-coloured solution in about ½ hour. After 1 hour at room temperature the mixture was heated at 60° for 5 minutes, boiled for 2 minutes, and then cooled in melting ice. Methyl iodide (5 g.; *ca.* 2 mols.) was then added and there was no obvious immediate reaction, although gradually the appearance of the mixture changed. After 15 hours at room temperature and 2·5 hours at the boiling point, a further quantity (1·6 c.c.) of methyl iodide was added and the mixture was allowed to simmer for a further 3·5 hours. The solution, from which potassium iodide had not separated apparently owing to its being held in colloidal suspension, was cooled and mixed with ether and water and the washed and dried ethereal solution was evaporated. When the crude product (5·1 g.) was distilled under diminished pressure, a light yellow, viscous oil (4·4 g.) collected, mainly at 175—185°/0·09 mm., with a small amount up to 200° owing to slight superheating; $n_D^{15°}$ 1·5508. On redistillation through a short column, there were obtained: (1) 1·0 g. of an almost colourless, viscous liquid, b. p. up to 180°/0·13 mm., and (2) 2·7 g. of a very viscous liquid, b. p. 180—192°/0·13 mm., $n_D^{14·5°}$ 1·5480 (Found: C, 72·5; H, 8·0. $C_{19}H_{24}O_4$ requires C, 72·2; H, 7·6%). The substance gave no ferric reaction in alcoholic solution and, as stated in the introduction, will be further examined in detail.

The authors thank the Royal Commission for the Exhibition of 1851 for a Senior Studentship awarded to one of them.

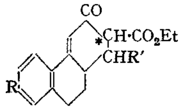
The Dyson Perrins Laboratory, Oxford University. [*Received, April 2nd*, 1936.]

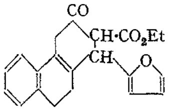
172. *Experiments on the Synthesis of Substances Related to the Sterols. Part X. Condensation of Furfurylidenetetralone with Ethyl Acetoacetate, and Analogous Studies.*

By D. A. Peak, Robert Robinson, and James Walker.

Knoevenagel's synthesis of *cyclo*hexenones from ethyl acetoacetate and unsaturated ketones can be applied to the preparation of potential intermediates for oestrone and analogous substances and the value of this route is being estimated in several directions in this laboratory.

Substances of the type (I) should be obtainable by one of two alternative methods: (*a*) by condensation of an alkylidene (or arylidene)-α-tetralone with ethyl acetoacetate, which is an adaptation of the normal known process, and (*b*) by the condensation of an α-tetralone with an alkylidene (or arylidene) derivative of ethyl acetoacetate.

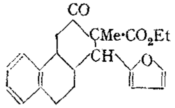
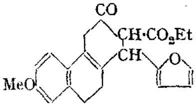
(I.) 

 (II.)

Suppose, for example, that R is MeO and R′ is $\cdot CH_2CH_2\cdot CO_2Et$; then methylation at the asterisked carbon atom, reduction of the *cyclo*hexanone ring, and ketonisation should afford the methyl ether of a stereoisomeride of oestrone. This attractive scheme has not yet been realised because 6-methoxy-2-γ-carbethoxypropylidene-α-tetralone could not be obtained by the condensation of 6-methoxytetralone with ethyl β-formylpropionate and 6-methoxytetralone could not be condensed with *ethyl γ-carbethoxypropylideneacetoacetate*, $CH_3\cdot CO\cdot C(CO_2Et){:}CH\cdot CH_2\cdot CH_2\cdot CO_2Et$ (III). Further experiments in these directions are in progress, but in the meantime we have also examined simpler cases in which the group

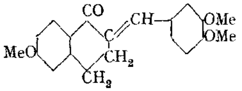
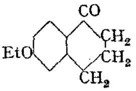
R′ could be suitably modified at the appropriate stage. For example, the furyl radical has been employed because it could be oxidised to carboxyl or even form the source of a side chain terminated by a carboxyl group.

We have obtained (I; R = H, R′ = C_4H_3O) from ethyl furfurylideneacetoacetate and α-tetralone and, better, from 2-*furfurylidene-α-tetralone* and ethyl acetoacetate. In the latter reaction sodium ethoxide is used as a catalyst in alcoholic solution and the first product is a bright yellow substance, which is gradually changed by the action of the reagent into an almost colourless isomeride. The yellow *α-form* is considered to be an αβ-unsaturated ketone (I) and the *β-form* is probably (II). Neither form can be directly *C*-methylated and the *β-form* is resistant to catalytic hydrogenation. The yellow α-variety affords, however, a *dihydro*-derivative and this has been methylated to the *keto-ester* (IV).

(IV.)   (V.)

The extension to the 6-*methoxy-2-furfurylidene-α-tetralone* series has been commenced, but the product of condensation of this substance with ethyl sodioacetoacetate is probably (V) because it is not smoothly hydrogenated in the presence of a catalyst. The anticipated volume of the gas was slowly absorbed, but the unchanged ester was recovered in large relative amount. Evidently a portion of the product suffers hydrogenation of one or both of the aromatic nuclei. We shall return to this subject when further supplies of γ-*m*-methoxyphenylbutyric acid are available, the line of work adumbrated in Part IX (preceding paper) having priority.

We have also had occasion to prepare 6-*methoxy-2-veratrylidene-α-tetralone* (VI) from 6-methoxytetralone and veratraldehyde by condensation in the usual manner in ethyl-alcoholic solution in the presence of sodium hydroxide. The apparently homogeneous product gave consistently high values for carbon content and many recrystallisations failed to remove the impurity.

(VI.)   (VII.)

The results suggested replacement of a methoxyl by an ethoxyl group and when methyl alcohol was used as solvent the analytical results were in perfect agreement with the anticipations of theory. Hence we prepared 6-*ethoxy-α-tetralone* (VII) and condensed it with veratraldehyde in ethyl-alcoholic solution. The resulting 6-*ethoxy-2-veratrylidene-α-tetralone* gave perfect analytical data, but was *not identical* with the abnormal compound mentioned above. The m. p.'s of these substances are grouped within a small range and mixtures show only small depressions; hence we conclude that exchange of alkoxyl does in fact occur in the reactive states of the molecules, but it is probably not confined to the 6-position in the tetralone nucleus.

Experimental.

Ethyl β-Formylpropionate.—Contrary to Wislicenus, Böklen, and Reuthe (*Annalen*, 1908, 363, 353) and in agreement with Sugasawa (*J. Pharm. Soc. Japan*, 1926, No. 534, 64; *Chem. Zentr.*, 1927, I, 1463) hydrolysis of ethyl hydroxymethylenesuccinate by means of water yields ethyl β-formylpropionate and not the free acid.

Ethyl hydroxymethylenesuccinate (100 g.) (Wislicenus, Böklen, and Reuthe, *loc. cit.*, p. 347) was heated with distilled water (250 c.c.) containing sodium acetate (1·0 g.) in an autoclave at 130—150° for 1½—2 hours. Care was taken to protect the liquid from contact with the walls and thermometer stem of the autoclave during the hydrolysis, as the yield was greatly diminished if this precaution was not observed. The product was taken up in ether after saturation of

the aqueous layer with sodium chloride and the extract was dried over sodium sulphate and evaporated. The aldehydo-ester had b. p. 82—95°/10 mm. (practically all at 82—87°) (yield, 50 g.), $n_D^{14°}$ 1·425, and was a colourless mobile oil having a characteristic odour.

Ethyl γ-Carbethoxypropylideneacetoacetate (III).—(A) A mixture of ethyl β-formylpropionate (1·7 g.), ethyl acetoacetate (1·8 g.), and acetic anhydride (1·9 g.) was maintained at 100° for 22 hours. The residue after removal of the acetic anhydride by distillation up to 140° at the ordinary pressure was fractionated under reduced pressure, *ethyl γ-carbethoxypropylideneacetoacetate* (1·4 g.) passing over as a faintly yellow, limpid oil at 160—168°/16 mm., $n_D^{14°}$ 1·4640 (Found: C, 58·1; H, 7·2%). The product gave a faint but definite pure blue colour in alcoholic ferric chloride, and this fact and the analysis suggested contamination with the saturated acetylated aldol.

(B) A mixture of ethyl β-formylpropionate (11·2 g.) and ethyl acetoacetate (11·8 g.) was cooled to − 10° and saturated with dry hydrogen chloride. After 15 hours at room temperature the mixture was added to water and extracted with ether. The extract was dried (anhydrous sodium sulphate) and evaporated. On fractionation of the crude product under reduced pressure there were obtained: (i) b. p. up to 150°/10 mm. (0·9 g.), (ii) b. p. 150—180°/10 mm. (16·5 g.). On further fractionation of (ii) the pure product (14·2 g.; 69% yield) was obtained, b. p. 168—170°/10 mm., as a faintly yellow, limpid oil, $n_D^{14°}$ 1·4645 (Found: C, 59·2, H, 7·2. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·4%). The product was halogen-free and gave no ferric reaction.

Attempted Condensation of Ethyl γ-Carbethoxypropylideneacetoacetate with 6-Methoxy-α-tetralone.—(A) The sodio-derivative of the ketone (8·8 g.) was prepared by means of sodamide (2·0 g.) and dry ether (100 c.c.) in the usual way, and the ester (12·1 g.) in ether (60 c.c.) was then slowly added with stirring. There was no evolution of heat nor any separation of a solid, but the reaction mixture became dark-greenish brown. After being stirred for 8 hours and kept at room temperature for 30 hours, the product was added to water and extracted with ether after acidification of the aqueous layer with acetic acid. The product isolated in the usual way was fractionated under reduced pressure, 6-methoxytetralone (7·2 g.) being recovered, possibly contaminated with some of the ester (the b. p.'s are practically coincident). On continued distillation decomposition set in and a very small fraction was collected at about 200°/0·2 mm. which, from the analysis, was not the desired product (Found: C, 64·2; H, 7·2. $C_{23}H_{28}O_6$ requires C, 69·0; H, 7·0%. Calc. for $C_{24}H_{32}O_8$: C, 64·3; H, 7·1%). This fraction gave a blue ferric reaction which gradually became violet.

(B) The ester (2·5 g.) and methoxytetralone (1·7 g.) were dissolved in absolute alcohol (25 c.c.) containing sodium ethoxide (0·3 g. of sodium). After being kept for 8 days at room temperature, the brown solution was added to water, acidified with acetic acid, extracted with ether, and worked up in the usual way. On distillation under reduced pressure a fraction (2·7 g.) consisting essentially of methoxytetralone was obtained, b. p. 160—175°/14 mm. There was a very small fraction distilling at *ca.* 210°/0·2 mm. which gave a red ferric reaction; it was not analysed or further examined.

Attempted Condensation of 6-Methoxytetralone with Ethyl β-Formylpropionate.—(A) The ketone (1·2 g.) and the aldehydo-ester (1·08 g.) were dissolved in absolute alcohol (15 c.c.) in which a trace of potassium had been dissolved. After 48 hours the ketone was recovered unchanged on passing into water.

(B) When a solution of the ketone (1·7 g.) and the aldehydo-ester (1·6 g.) in glacial acetic acid (2 c.c.) and acetic anhydride (0·5 c.c.) was saturated with dry hydrogen chloride at − 15°, a substance separated in prisms, the colour of which slowly deepened to reddish-orange and then red. After 15 hours the reddish-crimson prisms, which melted on access of moisture, gave a practically colourless oil on addition of water. This crystallised rapidly and on drying was found to consist of methoxytetralone (1·52 g.), m. p. 72—77°. The aqueous mother-liquor had a yellow colour and strong green fluorescence.

2-Furfurylidene-α-tetralone.—Aqueous sodium hydroxide (2 c.c. of 8%) was added to a solution of freshly distilled furfuraldehyde (11·2 g.) and α-tetralone (17 g.) in ethyl alcohol (50 c.c.). The liquid immediately darkened and after an hour had deposited a voluminous mass of pale yellow needles. After 12 hours the crystals were collected and washed with ethyl alcohol. The product (22·9 g.) had m. p. 75—76°, unaltered by recrystallisation (Found: C, 80·4; H, 5·3. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·3%). A further quantity (1·7 g.) was obtained by dilution of the mother-liquor with water. The *substance* was dimorphous, crystallising from alcohol in needles or in prisms, the latter being the stable form.

Condensation of Furfurylidenetetralone with Ethyl Sodioacetoacetate.—(A) Sodium (1·5 g.;

2 atoms) was dissolved in absolute alcohol (50 c.c.), ethyl acetoacetate (16·5 g.; 4 mols.) and furfurylidenetetralone (7 g.; 1 mol.) added, and the solution made up to 70 c.c. with absolute alcohol. The solution was then heated under reflux and 10 c.c. were withdrawn at periods of 15 mins., 30 mins., 1, 2, 3, and 4 hours from the commencement of heating. Each portion was made slightly acid with glacial acetic acid immediately after withdrawal, sufficient water added to redissolve the precipitated gelatinous sodium acetate, and the clear solution kept in the ice-chest for several hours. The crystalline products were then collected and washed with ethyl alcohol. Approximately the same quantity (0·2 g.) was obtained from each portion, but the initially formed substance (m. p. 117—118°) was golden-yellow and the final product was only faintly yellow (m. p. 118—119°, lowered by admixture with the former substance). Intermediate fractions showed a gradual decrease of colour intensity, the m. p. reaching a minimum (108—110°) in the 1-hour and 2-hour fractions and then rising again. They were, therefore, mixtures of the initial and the final product. Numerous experiments, in which the concentrations, temperature and time of reaction were varied and also in the presence of dehydrating agents such as aluminium ethoxide, have failed, as yet, to effect an increase in the yield of either substance (see below for an important by-product).

The first-formed product (*α-modification*) crystallised from ethyl alcohol and acetic acid in needles (labile form changing to plates) and prisms respectively, m. p. 119—120° (Found: C, 74·7; H, 6·1. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%). It was freely soluble in ether, moderately in ethyl acetate, and sparingly in cold ethyl alcohol and acetic acid. A green coloration developed on addition of ferric chloride to an alcoholic solution.

The end product (*β-modification*) crystallised from ethyl alcohol in faintly yellow needles, m. p. 120—121° (Found: C, 74·7; H, 6·1%). Its solubilities in most solvents were very similar to those of the α-modification, but it gave a violet ferric reaction. The faint colour, which could not be removed by repeated crystallisation, was evidently due to traces of the α-modification, since reduction with zinc and acetic acid or aluminium amalgam and absolute ethyl alcohol gave a colourless product, m. p. 121—122° alone or mixed with unreduced material (Found: C, 74·7; H, 6·1%). Further reduction either by catalytic or by other methods was not found possible.

(*B*) Ethyl sodioacetoacetate was prepared from powdered sodium (1·5 g.; 2 atoms) and ethyl acetoacetate (9 g.; > 2 mols.) in dry ether (80 c.c.) and a solution of furfurylidenetetralone (7 g.; 1 mol.) in dry ether (100 c.c.) was then added. The solution was refluxed for 18 hours; the sodio-derivative then disappeared and a clear yellow solution resulted. An equal volume of water was added and the ethereal layer was separated, dried, and concentrated to 20 c.c. Crystallisation soon commenced and the golden-yellow product (1·35 g.) melted at 115—116° alone or mixed with the α-modification. The ether was completely removed from the mother-liquor, and the residue taken up in a little alcohol. The solution first deposited unchanged furfurylidenetetralone (1·5 g.) and then further crops, all of which were mixtures of unidentified constituents.

(*C*) α-Tetralone (14·6 g.) was converted into its sodio-derivative in dry dioxan (nitrogen) by means of sodamide (3·9 g.). Ethyl furfurylideneacetoacetate (20·8 g.), b. p. 160—165°/1·5 mm., was added. Subsequently the α-modification (1·1 g.) of the above ester could be isolated, m. p. 116° alone or mixed with an authentic specimen.

3-*Keto*-1-*furyl*-1 : 2 : 3 : 4 : 9 : 10-*hexahydrophenanthrene*.—Furfurylidenetetralone and ethyl sodioacetoacetate were condensed in the same proportion as above (A) by heating for 30 minutes, yielding the α-modification (1·8 g.). The mother-liquor was diluted with water, and the resultant oil isolated by means of ether; it distilled as a pale yellow, viscous liquid (3·0 g.), b. p. 200—220°/3 mm. The *substance* crystallised in contact with ethyl alcohol and was recrystallised from this solvent, separating in almost colourless prisms, m. p. 113—114° (Found: C, 81·8; H, 6·0. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·0%). The same substance was produced on hydrolysis of the β-modification (above) with dilute aqueous-alcoholic sodium hydroxide. Obtained by this method, it was colourless, m. p. 114—115° alone or mixed with the above (Found: C, 82·0; H, 6·1%). It is therefore probably also a βγ-unsaturated ketone and it is important to note that this substance is the main product of the condensation reaction.

Ethyl 3-*Keto*-1-*furyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-2-*carboxylate*.—A 2% palladised strontium carbonate catalyst (0·5 g.) was shaken with ethyl acetate (10 c.c.) in hydrogen at atmospheric pressure until it was completely reduced. A solution of ethyl ketofurylhexahydrophenanthrenecarboxylate (0·38 g.) in ethyl acetate (10 c.c.) was then added, and the shaking continued; absorption of hydrogen (1 mol.) rapidly took place. The filtered ethyl acetate solution was evaporated; the residue crystallised on cooling. Recrystallised

from ethyl alcohol, the *substance* separated in colourless square plates, m. p. 134·5—135·5° (Found: C, 74·6; H, 6·5. $C_{21}H_{22}O_4$ requires C, 74·6; H, 6·5%). The ferric coloration in alcohol was pale brown.

Ethyl 3-Keto-1-furyl-2-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene-2-carboxylate (IV).—The last-described ester (3·0 g.) in dry benzene (60 c.c.) was heated with finely powdered potassium (0·4 g.) for 3 hours; the metal gradually disappeared and a clear yellow solution was obtained. Methyl iodide (3 g.) was then added and refluxing continued until the solution was almost decolorised and exhibited a neutral reaction towards litmus (12 hours). The precipitated potassium iodide was washed out with water, the benzene removed, and the residue, which crystallised in contact with ethyl alcohol, taken up in this solvent (10 c.c.). The solution deposited first unchanged material (1·4 g.) and then a crop (1·0 g.) of a different *substance*. This was recrystallised from ethyl alcohol, separating in hexagonal prisms, m. p. 93—93·5° (Found: C, 75·4; H, 6·8; OEt, 12·4. $C_{22}H_{24}O_4$ requires C, 75·0; H, 6·8; OEt, 12·8%). Further small quantities of this substance were gradually deposited by the mother-liquors. The ester gave no coloration with ferric chloride in alcoholic solution.

6-Methoxy-2-α-furfurylidene-α-tetralone.—This derivative was prepared in the same manner as furfurylidenetetralone, 6-methoxy-α-tetralone being used. It crystallised from alcohol in pale yellow needles, m. p. 104·5° (Found: C, 75·7; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

Ethyl 3-Keto-7-methoxy-1-α-furyl-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene-2-carboxylate (V).—A mixture of furfurylidenemethoxytetralone (12·5 g.), ethyl acetoacetate (26 g.), and alcoholic (100 c.c.) sodium (4·6 g.) ethoxide was refluxed for 4 hours, kept for 12 hours, and again refluxed for 3 hours. The sticky product obtained after the addition of water and acetic acid was well washed with water to remove unchanged ethyl acetoacetate, dissolved in alcohol, and kept in the ice-chest. The crystals obtained (5·6 g.) were a mixture, the main constituent being a *substance*, m. p. 137—138° after many recrystallisations (Found: C, 72·6; H, 6·1; MeO, 15·3%). The mother-liquor was kept in the ice-chest and deposited soft colourless crystals (6·2 g.), which, unlike the compound first isolated, developed a brownish-violet coloration with ferric chloride in alcoholic solution. This *substance* separated from alcohol in colourless matted needles, m. p. 122° (Found: C, 72·2; H, 5·9. $C_{22}H_{22}O_5$ requires C, 72·1; H, 6·0%). When it was shaken in hydrogen with ethyl acetate and a good platinum catalyst, 2·32 g. absorbed 315 c.c. in 5 hours. The isolated product crystallised from methyl alcohol as aggregates of very small, colourless needles, m. p. 112° (Found: C, 72·6; H, 6·3%). The m. p. was very slowly raised by crystallisation to about 118° and it was raised by admixture with the original ester, m. p. 122°. About half the product remained in the mother-liquor as an uncrystallisable oil. It is probable that dehydrogenation accompanied hydrogenation in this experiment.

6-Methoxy-2-veratrylidene-α-tetralone.—The product of condensation of veratraldehyde and methoxytetralone in ethyl-alcoholic solution, with 5*N*-aqueous sodium hydroxide as the catalyst, crystallised from ethyl alcohol in yellow flat needles or leaflets, m. p. 110—111° (Found: C, 74·7, 74·3, 74·6; H, 6·6, 6·4, 6·5. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%. $C_{21}H_{22}O_4$ requires C, 74·6; H, 6·5%). Material of this type was condensed with ethyl sodioacetoacetate under conditions similar to those used in other cases and a ferric-negative product was isolated in soft, colourless, prismatic needles, m. p. 123—124° by crystallisation from alcohol. We are unable to interpret the analysis (Found: C, 72·3; H, 6·3; MeO, 28·2%).

When the preparation was performed in methyl-alcoholic solution (see p. 753), the *product* crystallised in better-defined and longer, paler yellow needles, m. p. 111—112°, giving excellent analytical data (Found: C, 74·1, 74·3; H, 6·2, 6·4. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

6-Ethoxy-α-tetralone (VII).—The preparation of this substance was carried out by Mr. J. Resuggan. *m*-Ethoxybenzaldehyde (105 g.) (Werner, *Ber.*, 1895, **28**, 2001) was condensed with malonic acid (190 g.) in pyridine (450 c.c.) and piperidine (6 c.c.) for 4 hours on the steam-bath. The acid crystallised from 90% alcohol in long prismatic needles (135 g.), m. p. 129—130° (Werner, *loc. cit.*, gives m. p. 122°). A mixture of this acid (130 g.), toluene (400 c.c.), and 10% ethyl-alcoholic sulphuric acid (300 c.c.) was refluxed for 5 hours. The resulting *ester* (125 g.) had b. p. 158°/1 mm. and $n_D^{10°}$ 1·556 (Found: C, 70·9; H, 7·2. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). Reduction under the usual conditions with hydrogen and a 2% palladised strontium carbonate catalyst furnished *ethyl* β-m-*ethoxyphenylpropionate* (yield, quantitative), b. p. 148°/0·2 mm., $n_D^{10°}$ 1·502 (Found: C, 70·3; H, 8·1. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%). This ester (55 g.) in anhydrons alcohol (450 c.c.) was reduced by means of sodium (36·5 g.) at 160°. γ-m-*Ethoxyphenylpropyl alcohol* was obtained in 82% yield (Found: C, 73·4; H, 8·9. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%), b. p. 130°/3 mm., $n_D^{10°}$ 1·526. [It has been observed (J. R.) that there

is no increase in the yield in the Bouveault–Blanc reductions in this series when the amount of sodium employed exceeds 4 atoms; in fact the optimum yields are obtainable with rather less than the theoretically required quantity of the metal.] On treatment with thionyl chloride and dimethylaniline in the usual manner this alcohol (68 g.) afforded γ-m-*ethoxyphenylpropyl chloride* (70 g.), b. p. 111°/1 mm., $n_D^{19°}$ 1·525 (Found: C, 66·7; H, 7·7. $C_{11}H_{15}OCl$ requires C, 66·5; H, 7·6%). Again following the methoxy-series, the chloride (68 g.) was converted through the *nitrile* (60 g.), b. p. 127°/0·6 mm., $n_D^{19°}$ 1·519 (Found: C, 76·5; H, 8·1. $C_{12}H_{15}ON$ requires C, 76·2; H, 7·9%), into γ-m-*ethoxyphenylbutyric acid* (61 g.), which formed leaflets, m. p. 65—66°, from light petroleum (Found: C, 69·2; H, 7·8. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). The related amide (2 g.) was obtained by crystallisation of the residue from the distillation of the nitrile; m. p. 84—85° after deposition from benzene.

The ethoxyphenylbutyric acid (58 g.) was heated with a mixture of sulphuric acid (400 c.c.) and water (230 c.c.) for 20 minutes on the steam-bath. Purified in the usual manner, the product (37 g.) eventually crystallised from light petroleum in colourless prisms, m. p. 46—47° (Found: C, 75·8; H, 7·6. $C_{13}H_{14}O_2$ requires C, 75·8; H, 7·4%).

The *veratrylidene* derivative crystallised from alcohol in pale yellow plates, m. p. 119—120° (Found: C, 74·5; H, 6·6. $C_{21}H_{22}O_4$ requires C, 74·6; H, 6·5%). A mixture with pure veratrylidenemethoxytetralone had m. p. 110—112° and the same value was found for the mixture with presumed veratrylidenemethoxytetralone prepared in ethyl-alcoholic solution.

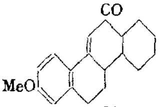
THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, April 2nd, 1936.*]

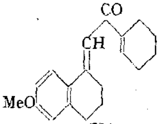
173. *Experiments on the Synthesis of Substances Related to the Sterols. Part XI. The Constitution of the Condensation Products from Acetyl*cyclo*pentene or Acetyl*cyclo*hexene and Methoxytetralone.*

By (MISS) D. M. CROWFOOT, WILLIAM SAGE RAPSON, and ROBERT ROBINSON.

CERTAIN examples of the new synthetic process described in Part II (J., 1935, 1285) are of especial interest in view of the close constitutional relation of the products with the female sex-hormones and also because favourable yields are obtainable from accessible materials. Cook and Hewett (this vol., p. 64), whilst admitting that these substances "probably contain condensed hydroaromatic systems," remark that the structures of the products have not been proved.

Nevertheless, the only alternatives to our suggested formulæ are inherently improbable. For example, in the condensation of 6-methoxy-α-tetralone with acetyl*cyclo*hexene the


(I.)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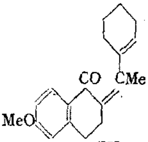
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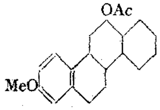
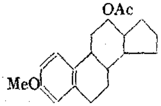
possibilities are (I), (II), and (III), of which (I) was selected. The expressions (II) and (III) were excluded because the general properties of the product were not in good agree-

(IV.)



(V.)

ment with such formulations and also for the specific reason that catalytic reduction afforded a tetrahydro-derivative of alcoholic rather than ketonic function. The prepar-

ation of the acetyl derivatives (IV) and (V) was actually carried out before Part II was published, although the absence of ketonic behaviour of the tetrahydro-derivatives was already patent. The *X*-ray crystal analysis is in harmony with the proposed structures, which are further confirmed by the results recorded in the two succeeding parts of this series.

EXPERIMENTAL.

2-*Acetoxy*-10-*methoxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene* (IV).—The hydrogenation product of ketomethoxydecahydrochrysene (Part II, *loc. cit.*) does not react with Brady's reagent, although all ketones of this series do so with facility. On heating with acetic anhydride for 3 hours on the steam-bath, the *acetate* was obtained; this crystallised from methyl alcohol in glistening needles, m. p. 155—156° (Found : C, 76·9; H, 8·5. $C_{21}H_{28}O_3$ requires C, 76·8; H, 8·5%). The corresponding methoxy*cyclo*pentanophenanthrene *derivative* (V), obtained in a similar fashion, crystallised from methyl alcohol in slender needles, m. p. 102—103° (Found : C, 76·4; H, 8·3. $C_{20}H_{26}O_3$ requires C, 76·4; H, 8·3%).

Crystallographic Data.—3-*Hydroxy*-7-*methoxy*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-*cyclopentanophenanthrene* (alcohol related to the acetate V). This compound formed needles much elongated along the *b* axis and flattened on (001). The extinction was straight with α along *b* and γ inclined at about 21° to the normal to the *c* plane.

The unit cell dimensions were : $a = 7·5$, $b = 5·3$, $c = 35·1$ A., $\beta = 98°$; *h*0*l* halved for *l* odd; 0*k*0 halved for *k* odd; space group, $P2_1/c$; $n = 4$ if $\rho = 1·29$.

The optical data and intensities suggest that the molecules are arranged as a four-layer structure in the *c* plane, the long axis being mainly along γ and the short axis somewhat inclined to the *b* plane.

The structure is of particular interest since it requires the presence of two identical pairs of molecules related by a glide plane of symmetry, that is, of pairs of enantiomorphous molecules.

2-*Hydroxy*-10-*methoxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene* (alcohol related to the acetate IV). From methyl alcohol this substance afforded long needles which rapidly became opaque on exposure to air. They therefore probably contained solvent of crystallisation and were not further investigated.

From light petroleum three forms separated :

A. Large, very fine tetragonal crystals showing well-developed prism and pyramid faces; optically they were positive.

The *X*-ray measurements gave : $a = 15·6$, $c = 12·8$ A.; *hkl* absent for $h + k + l$ odd; $n = 8$ for $\rho = 1·21$. There are no planes of symmetry and the space group is probably $I4$ or $I\bar{4}$. This is a very unusual type of crystal structure. The molecules are probably fitted into the cell with their long axes along *c* and short axes parallel or nearly so to *a*, since the 200 and 400 reflections are very powerful.

B. Very long needles. These very fine needles, mnch elongated along *a*, showed a crossed extinction as usually viewed, but straight at right angles to this direction. It was difficult to determine exactly the optic orientation, but α is probably at about 30° to the *a* axis.

The dimensions of the unit cell are : $a = 5·2$, $b = 24·7$, $c = 14·7$ A., $\beta = 128°$; $a \sin \beta = 4·1$; $c \sin \beta = 11·5$ A.; 0*k*0 absent for *k* odd; space group, $P2_1$; $n = 4$ for $\rho = 1·27$. There are two molecules in the asymmetric unit and the arrangement is probably such that thickness is mainly in the *a* plane and length along *b*. There seems no simple connexion between this and A.

C. This form consisted of small needles elongated along *b* and flattened on (100). Optically it appeared orthorhombic or pseudo-orthorhombic with α along *b*, β in *a* and γ in *c*. The crystals were very small and gave few *X*-ray reflections. It is almost certain that the true dimensions are some multiple of the following : $a = 14·6$, $b = 4·16$, $c = 14·0$ A.

That the three forms are truly polymorphic modifications of one and the same substance is indicated by the following observations. On crystallisation from methyl alcohol, only one type of crystal form was observed—the needle-shaped variety probably containing solvent. On melting, all three forms could be induced to pass into the same modification A. This was most difficult to obtain from C and was only observed after seeding. If A is kept melted for some time and then cooled suddenly, all three forms are occasionally produced. They are easily distinguished in polarised light, since in B the extinction appears crossed with reference to the needle axis and in A this axis is the slow extinction, in C the fast.

2-*Keto*-10-*methoxy*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 14 : 15 : 16-*decahydrochrysene* (I). This compound occurs as fine needles, very much elongated along *a*. All the crystals examined proved to be very close twins which although monoclinic simulated orthorhombic symmetry closely.

The dimensions of the monoclinic unit were: $a = 8{\cdot}3$ A. α, $b = 15{\cdot}65$ A. γ, $c = 12{\cdot}3$ A. β, β = 109°; $0k0$ absent for k odd; $h0l$ absent for $h + l$ odd (?). It is a little difficult to make sure of the halvings owing to the twin character of the crystals. Space group, $P2_1/n$; $n = 4$ for ρ = 1·22. The pseudo-orthorhombic cell formed by twinning has $a = 8{\cdot}3$, $b = 15{\cdot}65$, $c = 23{\cdot}8$ A.; hkl halved for $h + l$ halved.

Optically, in spite of the monoclinic symmetry, the extinction appeared straight along the needle. The birefringence was high, positive, and the optic axial angle small.

3-*Keto*-7-*methoxy*-3 : 9 : 10 : 11-*tetrahydro*-1 : 2-cyclo*pentanophenanthrene*. This is very similar to its ring homologue (I). The crystals are needles elongated along the a axis and showing a straight extinction. As in the case of (I), they are invariably twins simulating orthorhombic symmetry. The cell dimensions are probably as given below, but the crystals, being very small, gave very weak reflections and no planes observed indicated an a axis longer than 4·05 A.: $a = 8{\cdot}1$, $b = 14{\cdot}65$, $c = 12{\cdot}15$ A., β = 112°; $n = 4$ for ρ = 1·255. For the orthorhombic apparent cell: $a = 8{\cdot}1$ (/2), $b = 14{\cdot}65$, $c = 23{\cdot}70$ (/2), A. The optical character is exactly similar to that of (I) described above.

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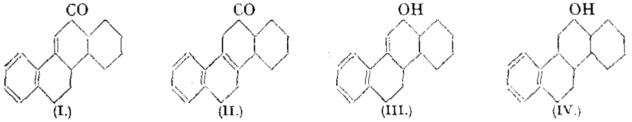
174. *Experiments on the Synthesis of Substances Related to the Sterols. Part XII. Some Hydrochrysene Derivatives.*

By D. A. PEAK and ROBERT ROBINSON.

THE condensation of sodio-α-tetralone with acetyl*cyclo*hexene under conditions similar to those prescribed in Part II (Rapson and Robinson, J., 1935, 1285) proceeds unusually smoothly and a *ketodecahydrochrysene-A* (I) is obtained in yields up to 80%. This substance has therefore been examined in detail. The mother-liquors from the first preparation of (A) afforded an isomeride (B), and a third isomeride (C) was isolated in a similar



(I.) (II.) (III.) (IV.)

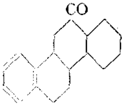
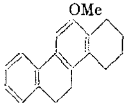
way in subsequent experiments. The substances (A), (B), and (C) are undoubtedly distinct chemical individuals and not mixtures; their melting points are widely separated and mixtures showed large depressions.

Mr. A. E. Gillam of the Chemistry Department of the University of Manchester has kindly reported on the absorption spectra of these isomerides. (A) and (B) show identical absorption, which is similar to that characteristic of benzylideneacetone; (C) gives entirely different results indicating that the unsaturated group is no longer conjugated with the carbonyl. Hence (A) and (B) are stereoisomerides (I) and the formula (II) is the best that can be attributed to (C). Unfortunately the isomerides (B) and (C) were accessible in such small quantities that their transformations could not be fully examined.

An attempt to convert (A) into (C) was made by refluxing the substance with alcoholic sodium ethoxide, but the outcome was remarkable because the product was the unsaturated *alcohol* (III), which yields a *phenylurethane*. A parallel for this reaction in a very different region of organic chemistry may be found in the reduction of diacetyldeuteroporphyrin (Fischer and Zeile, *Annalen*, 1929, **468**, 98). Catalytic reduction of (I)-A yields a *hydroxydodecahydrochrysene-α* (IV), and an isomeride (β) is produced when reduction is effected by means of sodium and alcohol. In this case the isomerism is concerned with the configuration of the *sec.*-alcohol group and *isomeride-α* can be converted into the β-form by treatment with *iso*amyl-alcoholic sodium *iso*amyloxide.

On oxidation with chromic acid the α- and the β-form gave one and the same *ketone* (V). This substance could not be converted into a benzylidene derivative, doubtless as the result of real steric hindrance.

An attempt to methylate the ketone by means of sodamide and methyl iodide was fruitless, but when the unsaturated ketone (I)-A was similarly treated a methoxyl-containing compound, probably (VI), was obtained.

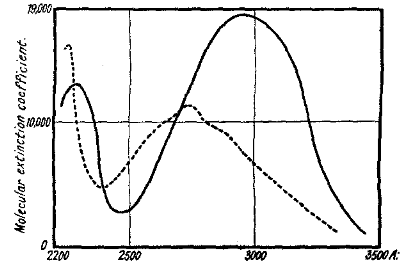
(V.)   (VI.)

The Clemmensen reduction of (I)-A furnished a decahydrochrysene which was doubtless a mixture, whereas a homogeneous *decahydrochrysene* was obtained by applying the Wolff–Kishner method to the saturated ketone (V). This decahydrochrysene gave chrysene when it was heated with selenium at 310—320°.

Finally it is interesting that the unsaturated ketone (I)-A also afforded chrysene when it was heated with selenium. A by-product of this reaction was a *substance*, $C_{18}H_{12}O$. This reduction of a carbonyl group in a selenium dehydrogenation process is not unique; it has been observed in the phenanthrene series and is perhaps due to the powerful reducing properties of the intermediate products of the dehydrogenation.

Experimental.

2-*Keto*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 14 : 15 : 16-*decahydrochrysene-A* (I).—Sodio-α-tetralone was prepared from α-tetralone (15·7 g.) (Hock and Susemihl, *Ber.*, 1933, **66**, 61) and finely powdered sodamide (4·2 g.) in anhydrous ether (200 c.c.) with stirring at room temperature for 7 hours,



Ketodecahydrochrysenes : ——— *Isomerides A and B.*
------ *Isomeride C.*

ammonia being removed in a stream of dry oxygen-free nitrogen, and finally by gentle refluxing for 1 hour. Acetyl*cyclo*hexene (13·3 g.) (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1157), dissolved in ether (20 c.c.), was then added drop-wise with stirring and ice-cooling. After 12 hours the crystalline mass which had separated was collected after addition of dilute sulphuric acid and washed with alcohol and ether. The crude *product* (19·0 g.; 70% yield) after one recrystallisation from ethyl alcohol (1000 c.c.) was pure. It separated from this solvent in glistening needles, m. p. 200—200·5° (Found: C, 85·5; H, 7·9. $C_{18}H_{20}O$ requires C, 85·7; H, 7·9%), or from dilute solutions in large square plates which on recrystallisation reverted to the needle form. Both forms appeared stable, no interchange being observed when mixtures of the crystals were left for several weeks in contact with alcohol. The substance was sparingly soluble in all solvents except hot alcohol, ethyl acetate, and acetone.

In subsequent condensations by refluxing the reaction mixture for 2 hours after the initial reaction at room temperature for 12 hours, the yield was as high as 80%.

2-*Keto*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 14 : 15 : 16-*decahydrochrysene-B* (I).—In the initial condensation, the ethereal solution on concentration deposited a second substance (0·9 g.) more readily soluble in all solvents than the first substance. It was recrystallised several times from alcohol, separating in fine needles, m. p. 152—153° (Found : C, 85·8 ; H, 8·0%). The m. p. was much depressed on admixture with the isomeride A.

2-*Keto*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 15 : 16-*decahydrochrysene-C* (II).—Subsequent condensations yielded none of the isomeride B. The residue after complete removal of the ether gave a small fraction, b. p. 190—210°/2 mm., which partly crystallised in contact with ether. It was recrystallised several times from ethyl alcohol, aqueous methyl alcohol, and aqueous acetone, separating in small needles, m. p. 115—115·5° (Found : C, 86·0 ; H, 8·2%). The substance was more readily soluble in all solvents than isomerides A and B and its m. p. was considerably depressed by addition of either of the latter.

Substance.	Absorption spectrum.	Molecular extinction coefficient, ϵ.
A	One broad band, max. 2960 A. (min. 2460 A.) and a second indefinite band at 2290 A.	18,650
B	,, ,, ,,	18,650
Benzylideneacetone.	One broad band, max. 2850 A.	23,000
Phenyl styryl ketone	One band at 3100 A., min. 2460 A.	26,000
C	Broad band with incipient narrow bands on either side of main maximum.	10,600
	Inflexion, 2640 A. Main max., 2750 ,, Inflexion, 2860 ,, 1 minimum, 2390 ,,	10,600

Attempted Methylation of 2-Ketodecahydrochrysene-A. Isolation of 2-Methoxy-3 : 4 : 5 : 6 : 7 : 8-hexahydrochrysene (VI ?)—The sodio-derivative of the unsaturated ketone (3·1 g.) was formed by refluxing it with sodamide (0·5 g. ; 1 mol.) in dioxan (100 c.c.), previously distilled from sodium and sodamide, until evolution of ammonia had ceased (3 hours). Methyl iodide (3·5 g. ; 2 mols.) was then added, and refluxing continued until the solution was neutral to moist litmus (3 hours). The filtered solution was concentrated to 10 c.c. and yielded unchanged material (0·6 g.) together with an uncrystallised residue, b. p. 190—200°/3 mm. The distillate partly crystallised in contact with ether, yielding further unchanged material (0·4 g.). The residue then gradually crystallised from aqueous alcohol, yielding a *substance* (0·25 g.) which, recrystallised from ethyl or methyl alcohol, gave well-formed long plates, m. p. 95·5—96° (Found : C, 86·2 ; H, 7·4 ; OMe, 10·8, 10·8. $C_{19}H_{20}O$ requires C, 86·4 ; H, 7·6 ; OMe, 11·7%).

2-*Hydroxy*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 14 : 15 : 16-*decahydrochrysene*.—2-Ketodecahydrochrysene-A (3 g.) was refluxed with a solution of sodium (5 g.) in absolute alcohol (50 c.c.) for 7 hours. The deep red liquid was mixed with water and extracted with ether. The residue after removal of the ether had b. p. 216—218°/3 mm. The light yellow, vitreous mass (1·9 g.) crystallised in contact with ether and then separated from 50% aqueous ethyl alcohol in small colourless needles, m. p. 136° (Found : C, 85·0 ; H, 8·7. $C_{18}H_{22}O$ requires C, 85·0 ; H, 8·7%). The *substance* was extremely soluble in the usual organic solvents. Its *phenylurethane* crystallised from ethyl alcohol in needles, m. p. 173—173·5° (Found : C, 80·4 ; H, 7·3. $C_{25}H_{27}O_2N$ requires C, 80·4 ; H, 7·3%).

2-*Hydroxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene*-α (IV).—The unsaturated ketone (I)-A (9·9 g.) was hydrogenated in ethyl-alcoholic suspension (250 c.c.) by shaking with a 2% palladium–strontium carbonate catalyst (3 g.) for 10 hours in hydrogen at 3 atm. pressure. The catalyst along with unchanged material (1·0 g.) was collected ; the filtrate on concentration to 10 c.c. slowly deposited crystals (4·0 g.), which separated from aqueous ethyl alcohol in fine needles, m. p. 114—115° (Found : C, 84·3 ; H, 9·1. $C_{18}H_{24}O$ requires C, 84·4 ; H, 9·4%). Further quantities of less pure material slowly separated from the mother-liquors. The *substance* was freely soluble in most organic solvents. The *phenylurethane* separated from alcohol in clusters of needles, m. p. 197—198° (Found : N, 3·6. $C_{25}H_{29}O_2N$ requires N, 3·7%).

When ethyl acetate was used as the solvent in this hydrogenation process, the main product was the *saturated* ketone (*q.v.*).

2-*Hydroxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene*-β (IV).—(1) The un-

saturated ketone (I)-A (5·0 g.) was dissolved in hot absolute alcohol (250 c.c.), and a large excess of sodium (25 g.) added in small pieces to the boiling solution. The alcohol was then removed under diminished pressure, and the residual solid decomposed with water (500 c.c.). The warm clear solution on cooling deposited clusters of needles (2·3 g.), which crystallised from 30% aqueous alcohol in fine small needles, m. p. 134—135° (Found : C, 84·3; H, 9·3%). The material was easily soluble in the cold in all common organic solvents and appreciably soluble in hot water. The *phenylurethane* separated from alcohol in needles, m. p. 197—198°, depressed by admixture with the isomeric phenylurethane (Found : N, 4·1%).

(2) The isomeride-α (0·2 g.) was heated with a solution of sodium (0·2 g.) in *iso*amyl alcohol (5 c.c.) for 2½ hours. The *iso*amyl alcohol was then removed in a current of steam, and the resultant oil collected by means of ether. The substance crystallised, and was recrystallised from aqueous ethyl alcohol. The product (0·1 g.) had m. p. 134—135° alone or when mixed with the isomeride-β.

2-*Keto*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene* (V).—The above isomeride-α (1·6 g.) was dissolved in cold glacial acetic acid (18 c.c.), and a solution of chromic acid (0·48 g.; 1 atom O) in glacial acetic acid (15 c.c.) added drop-wise with cooling and stirring. The chromic acid was completely reduced after 12 hours and a mass of crystals had separated. The mixture was heated on the water-bath for 30 minutes and then diluted with water (15 c.c.). On cooling, the *ketone* separated (1·2 g.). It was recrystallised several times from glacial acetic acid and ethyl alcohol, separating in long needles, m. p. 145—146° (Found : C, 85·6, 85·7; H, 8·9, 8·7. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%). A further quantity of less pure material (0·3 g.) was obtained by dilution of the acetic acid mother-liquors. The ketone was moderately soluble in most solvents, freely in hot ethyl alcohol and acetic acid. The *oxime* separated from ethyl alcohol in long needles, m. p. 220—221° (decomp.) (Found : C, 80·7; H, 8·5; N, 5·2. $C_{18}H_{23}ON$ requires C, 80·3; H, 8·6; N, 5·2%). The semicarbazone was almost insoluble in all solvents, and sparingly soluble in hot ethyl alcohol, from which it separated in small prisms, m. p. 223—224°.

The most rigorous conditions, for example, boiling the sodio-derivative in dioxan with benzaldehyde, failed to give a benzylidene derivative, but the substance gave indications of the presence of a keto-methylene group in the test with β-resorcylaldehyde.

On oxidation under identical conditions, the isomeride-β yielded a product shown by m. p. and undepressed mixed m. p. to be the same as that obtained from the isomeride-α.

Attempted Methylation of 2-Ketododecahydrochrysene.—The sodio-derivative was formed from the ketone (2·0 g.) and sodamide (0·3 g.) by refluxing in dry benzene (50 c.c.) until no more ammonia was evolved (8 hours). Excess (2·0 g.) of methyl iodide was then added, and refluxing continued until the solution gave a neutral reaction to moist litmus (36 hours). Water was then added, and the benzene layer evaporated to dryness. The residue was taken up in hot ethyl alcohol (15 c.c.); the solution on cooling depositing unchanged substance (0·8 g.). The residue after removal of the solvent was distilled under diminished pressure, and the distillate converted in an oxime which, after one recrystallisation, had m. p. 216—218° alone or mixed with the oxime of the original saturated ketone. The mother-liquors both from the formation of the oxime and from the recrystallisation contained no appreciable amounts of any second substance.

Decahydrochrysene.—2-Ketodecahydrochrysene-A (3 g.) was gently refluxed with amalgamated zinc (10 g.), concentrated hydrochloric acid (20 c.c.), and a few drops of anisole for 18 hours. A further addition of hydrochloric acid (2 c.c.) was made every 3 hours. The yellow semi-solid product was taken up in ether, the ethereal solution dried and evaporated, and the residue distilled, yielding 0·5 g. of a pale yellow, viscous liquid, b. p. 170°/3 mm. The residue could not be distilled without decomposition and probably consisted of polymerisation products. The distillate was freely soluble in ether, light petroleum and benzene, sparingly soluble in cold ethyl alcohol. It crystallised from ether–alcohol on long standing in the ice-chest and was recrystallised from ethyl alcohol, forming long fine needles, m. p. 87—91° with sintering from 83°. As this behaviour was unaffected by further crystallisation, the substance was probably a mixture either of stereoisomerides or of the $\Delta^{1:13}$- and the $\Delta^{13:14}$-componnd (Found: C, 90·5; H, 9·4. Calc. for $C_{18}H_{22}$: C, 90·8; H, 9·2%).

The crude semicarbazone of ketododecahydrochrysene (3 g.) was heated in a sealed tube with a solution of sodium (1·6 g.) in alcohol (20 c.c.) for 17 hours at 170°. The contents of the tube were then washed out with water, the flocculent white precipitate dissolved in ether, and the ethereal solution washed with water. On concentration of the ethereal solution to a small [illegible]

redistilled from sodium, and finally recrystallised from ethyl alcohol, separating in clusters of fine needles, m. p. 93—94° (Found: C, 90·8; H, 9·4. $C_{18}H_{24}$ requires C, 90·0; H, 10·0%. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%).

Chrysene.—(a) Decahydrochrysene (0·6 g.) and selenium powder (3·5 g.) were heated together at 310—320° for 18 hours, the crystalline sublimate being repeatedly pushed back into the melt to ensure complete dehydrogenation. The final sublimate (0·4 g.) was resublimed at 250° from sodium, and the white sublimate (0·3 g.) recrystallised from benzene, forming characteristic plates, m. p. 248° alone or mixed with authentic chrysene (Found: C, 94·7; H, 5·3. Calc. for $C_{18}H_{12}$: C, 94·7; H, 5·3%). The *s*.-trinitrobenzene complex crystallised from benzene in yellow needles, m. p. 185°; Sudborough (J., 1916, **109**, 1344) gives m. p. 186°.

(b) Decahydrochrysene (0·08 g.) on similar treatment with selenium (0·4 g.) gave 0·02 g. of pure chrysene.

Dehydrogenation of Ketodecahydrochrysene-A.—The unsaturated ketone (1·0 g.) was heated with selenium (5 g.) for 18 hours at 320°. The crude sublimate (0·95 g.) was dissolved in hot ethyl alcohol (200 c.c.) and boiled with charcoal for 2 hours, and the filtrate concentrated to 80 c.c. Part of the material (0·2 g.) crystallised in rhomboidal plates and was identified as chrysene after recrystallisation from alcohol and benzene. The mother-liquor on concentration yielded a second substance (0·25 g.), much more soluble in ether and alcohol than chrysene. It was separated from chrysene by solution in ether and filtration from the undissolved chrysene and after recovery was repeatedly crystallised from glacial acetic acid, from which it separated in large hexagonal plates, stout needles, or rhomboidal plates, m. p. 210—220° (decomp.) after darkening at 205° (Found: C, 88·7; H, 4·9. $C_{18}H_{12}O$ requires C, 88·5; H, 4·9%).

The authors thank the University of New Zealand for a Travelling Scholarship awarded to one of them.

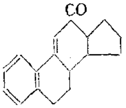
THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, April 2nd*, 1936.]

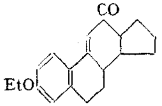
175. *Experiments on the Synthesis of Substances Related to the Sterols. Part XIII. Hydrocyclopentanophenanthrene Derivatives.*

By J. R. HAWTHORNE and ROBERT ROBINSON.

THE condensation of sodio-α-tetralone with acetyl*cyclo*pentene (Rapson and Robinson, J., 1935, 1287) does not proceed so smoothly as with acetyl*cyclo*hexene (preceding paper) and only one of the products has been isolated in a crystalline condition; there is a considerable uncrystallisable fraction which has not yet been fully investigated.

*Ketotetrahydro*cyclo*pentanophenanthrene* (I) has been reduced to a saturated *alcohol*

(I.) 

 (II.)

(*phenylurethane*), and the latter oxidised to a saturated *ketone*. The unsaturated ketone has also been reduced by the Wolff-Kishner method with formation of a *tetrahydro*-1 : 2-cyclo*pentanophenanthrene*.

6-Ethoxy-α-tetralone and acetyl*cyclo*pentene were condensed under the usual conditions with the formation of (II).

EXPERIMENTAL.

1-*Acetyl*cyclo*pentene* (cf. Rapson and Robinson, *loc. cit.*).—By maintaining the temperature below − 15° during the addition of the *cyclo*pentene and acetyl chloride the yield was increased to 50%. A longer period of heating with dimethylaniline at 180° gave a much purer product, b. p. 72—74°/12 mm. (Found: C, 76·4; H, 8·9. Calc. for $C_7H_{10}O$: C, 76·4; H, 9·0%). Attempts to add the elements of hydrogen chloride and hydrogen bromide to acetyl*cyclo*pentene

were only partly successful; the products decomposed on distillation and clear-cut fractions were not obtainable in adequate amount.

*3-Keto-3 : 9 : 10 : 11-tetrahydro-1 : 2-*cyclo*pentanophenanthrene* (I).—α-Tetralone (10 g.) (Hock and Susemihl, *Ber.*, 1933, **66**, 61), finely powdered sodamide (3 g.), and dry ether (140 c.c.) were refluxed with stirring in a current of dry oxygen-free hydrogen for 5 hours; the sodio-derivative had then separated as a pale yellow precipitate. Acetyl*cyclo*pentene (8 g.) was added to the hot reaction mixture and stirring and refluxing were continued for 1 hour. The sodio-derivative disappeared and the solution darkened. After 12 hours the mixture was kept in the ice-chest for a further 24 hours; the product then crystallised. Dilute sulphuric acid was added, and the crude product (3 g.) collected. The *substance* crystallised from alcohol in colourless needles, m. p. 169—170° (Found : C, 85·6; H, 7·5. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). From the ethereal layer there was obtained a viscous liquid (5 g.), b. p. 170—190°/0·065 mm. (mostly at 180—187°), and an alcoholic solution of this deposited only 0·5 g. of the above unsaturated ketone, m. p. 170°. The *oxime* separated from alcohol in glistening prisms, m. p. 235·5° (decomp.) (Found : C, 80·7; H, 7·2; N, 5·8. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·5; N, 5·5%).

*3-Hydroxy-3 : 4 : 9 : 10 : 11 : 12-hexahydro-1 : 2-*cyclo*pentanophenanthrene.*—Ketotetrahydro*cyclo*pentanophenanthrene (0·5 g.), methyl alcohol (50 c.c.), and a 2% palladised strontium carbonate catalyst (2 g.) were shaken together in hydrogen for 10 hours, and the filtered solution evaporated. The residue crystallised from aqueous alcohol in fine colourless needles, m. p. 106° (yield, 60%) (Found : C, 83·5; H, 9·2. $C_{17}H_{22}O$ requires C, 84·3; H, 9·0%). The low value for carbon is difficult to explain, but it could not be remedied. The *phenylurethane* was therefore prepared in order to confirm the composition of the substance. The alcohol (0·1 g.) and phenyl *iso*cyanate (0·05 g.) were heated together at 100° for 30 minutes. The derivative separated on the addition of light petroleum; it crystallised from alcohol in prisms, m. p. 175° (Found : C, 79·9; H, 7·6. $C_{24}H_{27}O_2N$ requires C, 79·8; H, 7·5%). The product of reduction of ketotetrahydro*cyclo*pentanophenanthrene with sodium and alcohol was an uncrystallisable viscous liquid.

*3-Keto-3 : 4 : 9 : 10 : 11 : 12-hexahydro-1 : 2-*cyclo*pentanophenanthrene.*—A solution of chromic acid (0·07 g.) in glacial acetic acid (2 c.c.) was gradually added to the above-described alcohol (0·25 g.) in glacial acetic acid (3 c.c.) with cooling and stirring. After 12 hours at room temperature, water was added. The *product* (yield, 75%) crystallised from aqueous alcohol in short colourless needles, m. p. 115—116·5° (Found : C, 84·8; H, 8·5. $C_{17}H_{20}O$ requires C, 85·0; H, 8·3%). The *semicarbazone* was only slowly formed in hot alcoholic solution. It separated from aqueous methyl alcohol in small plates, m. p. 191—192° (Found : C, 72·6; H, 7·5; N, 13·9. $C_{18}H_{23}ON_3$ requires C, 72·7; H, 7·7; N, 14·1%).

Under similar conditions of oxidation 3-hydroxy-7-methoxyhexahydro*cyclo*pentanophenanthrene (Rapson and Robinson, *loc. cit.*) was largely recovered unchanged.

*3 : 9 : 10 : 11-Tetrahydro-1 : 2-*cyclo*pentanophenanthrene.*—The semicarbazone of 3-keto-3 : 9 : 10 : 11-tetrahydro-1 : 2-*cyclo*pentanophenanthrene (2 g.) was heated in a sealed tube at 170° with alcoholic sodium ethoxide (1·6 g. sodium, 25 c.c. alcohol) for 17 hours. The *product* was isolated by means of ether and heated with sodium for 1 hour at 150°; it then distilled from sodium as a clear liquid, b. p. 164—165°/3 mm. (Found : C, 91·2; H, 9·0. $C_{17}H_{20}$ requires C, 91·1; H, 8·9%).

*3 : 4 : 9 : 10 : 11 : 12-Hexahydro*cyclo*pentanophenanthrene.*—A mixture of ketohexahydro*cyclo*pentanophenanthrene (2 g.), amalgamated zinc (20 g.), and concentrated hydrochloric acid (10 c.c.), was refluxed for 24 hours. The *hydrocarbon* was isolated, heated for ½ hour with sodium at 150°, and distilled; b.p. 201°/16 mm. (Found: C, 90·6; H, 9·6. $C_{17}H_{22}$ requires C, 90·3; H, 9·7%).

*1 : 2-*cyclo*Pentenophenanthrene.*—Dehydrogenation of 3-hydroxy-3 : 4 : 9 : 10 : 11 : 12-hexahydro*cyclo*pentanophenanthrene by means of palladised charcoal at 330° for 17 hours afforded a small amount of material, m. p. 152° after sublimation in a vacuum and crystallisation from alcohol. The nearly colourless leaflets may have consisted of a polymorphic form of the hydrocarbon, but the quantity was too small for further examination.

Hydroxyhexahydro*cyclo*pentanophenanthrene (0·5 g.), mixed with selenium powder (2·5 g.), was heated (bath at 310—320°) for 15 hours, any sublimate being returned to the melt. The powdered mass was extracted with alcohol, and the greenish-blue fluorescent solution concentrated. The material that separated was further purified by crystallisation from alcohol, adsorption on and elution from alumina, and crystallisation from light petroleum (b. p. 40—50°). The colourless needles had m. p. 135°, alone or mixed with an authentic specimen supplied by Dr. G. A. R. Kon, to whom we are very grateful.

3-Keto-7-ethoxy-3 : 9 : 10 : 11-tetrahydro-1 : 2-cyclopentanophenanthrene (II).—The sodio-derivative of 6-ethoxy-α-tetralone (Part X; this vol., p. 756) (9·5 g.) was prepared in boiling ethereal solution (100 c.c.) by means of powdered sodamide (2 g.) during 4 hours; air was displaced by nitrogen during this operation. Acetyl*cyclo*pentene (7 g., containing a little chlorine) was then added, and the mixture refluxed for 7 hours (nitrogen). A crystalline precipitate (5·3 g.) was collected after cooling, neutralisation with dilute hydrochloric acid, and keeping in the ice-chest. The *substance* crystallised from ethyl alcohol, in which it was sparingly soluble, in prismatic needles, m. p. 154—156° (Found: C, 80·6, 80·7; H, 7·8, 8·0; EtO, 16·2. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·8; EtO, 16·0%). No pure substance, other than a small further quantity of the main product, could be isolated from the ethereal mother-liquor by crystallisation, but, on distillation, ethoxytetralone was recovered (3 g.) and an oil of the approximate composition $C_{19}H_{22}O_2$ was also obtained (1·6 g.).

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176. *The Constitution of the Purine Nucleosides. Part IV. Adenosine and Related Nucleotides and Co-enzymes.*

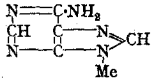
By J. MASSON GULLAND and ENSOR R. HOLIDAY.

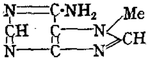
IN previous communications (*Nature*, 1933, **132**, 782; Part II, J., 1934, 1639) comparisons of the ultra-violet absorption spectra of aqueous solutions of xanthosine and monomethylated derivatives of xanthine at different p_H values provided evidence that in this nucleoside, in guanosine, and in the related nucleotides the pentose groups are attached to position 9 of the nitrogenous nucleus.

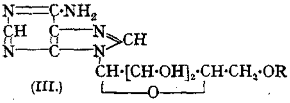
The method has now been extended to the determination of the constitutions of adenosine, obtained from yeast nucleic acid, and of inosine prepared from it by deamination with nitrous acid. The details of the constitutions of these nucleosides are known, except for the decision between positions 7 and 9 as the point of attachment of the ribose radical to the adenine and the hypoxanthine molecule.

It is clear from Figs. 1 and 2 and Table I that the spectra of adenosine very closely resemble those of 9-methyladenine (I) but not those of 7-methyladenine (II). Similarly, the spectra of inosine (from adenosine) resemble more closely those of 9-methylhypoxanthine than those of 7-methylhypoxanthine (Figs. 5 and 6).

The evidence presented above indicates that the ribose radicals of adenosine (III, R = H), inosine, and by inference adenosine-3-phosphoric acid of yeast nucleic acid, are attached to the 9-position of adenine and not to the 7-position, as is commonly represented. There is thus an interesting parallel between the nucleosides and flavine, in which the ribityl residue is attached to the corresponding nitrogen atom (v. Euler, Karrer, Malmberg, Schöpp, Benz, Becker, and Frei, *Helv. Chim. Acta*, 1935, **18**, 522; Kuhn, Reinemund, Weygand, and Ströbele, *Ber.*, 1935, **68**, 1765).


(I.)


(II.)


(III.)

Muscle Adenylic Acid and Co-enzymes.—The formulation of muscle adenylic acid as an adenine-riboside-5-phosphoric acid is fully established by the following series of changes: its deamination to inosinic acid, which yields hypoxanthine and ribose-5-phosphoric acid on hydrolysis by acid (Embden and Schmidt, *Z. physiol. Chem.*, 1929, **181**, 130; Levene and Jacobs, *Ber.*, 1911, **44**, 746; Levene and Stiller, *J. Biol. Chem.*, 1934, **104**, 299); the neutral hydrolysis of the barium salt of inosinic acid to barium phosphate and inosine (Levene and Jacobs, *Ber.*, 1909, **42**, 336); the preparation of inosine by deamination of adenosine (Levene and Jacobs, *Ber.*, 1910, **43**, 3161). These facts alone might also indicate that muscle adenylic acid is a derivative of yeast adenosine. This is indeed the case, as will be shown

below, and muscle adenylic acid has now been smoothly hydrolysed to adenosine by means of bone phosphatase; fission by chemical means is impracticable, since the phosphoric ester linkage is more stable to acid hydrolysis than is that of the riboside. Nevertheless the recognition of muscle adenylic acid as a 9-ribose derivative of adenine is based on the identification of the compounds in the reactions mentioned above, and this line of argument

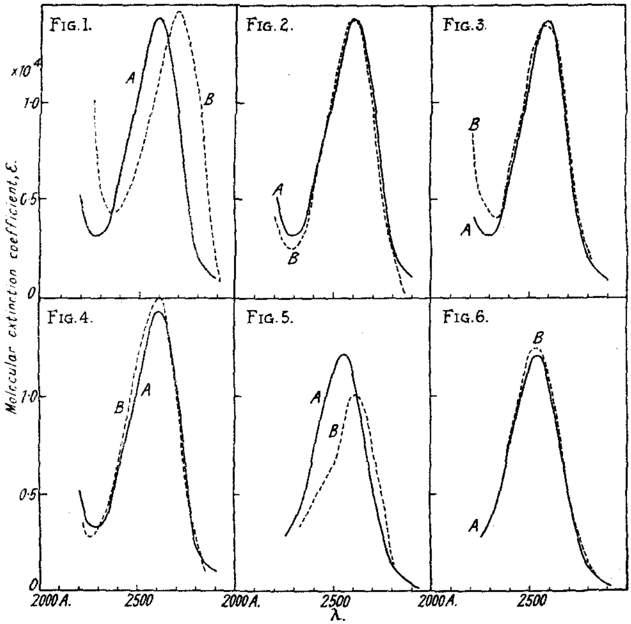


FIG. 1.—*A*. *9-Methyladenine in water, N/20-NaOH, and N/20-HCl.* *B*. *7-Methyladenine in water and N/20-HCl.*
FIG. 2.—*A*. *9-Methyladenine.* *B*. *Adenosine in water, N/20-NaOH, and N/20-HCl.*
FIG. 3.—*A*. *9-Methyladenine.* *B*. *Muscle adenylic acid in water at p_H 4·5, in N/20-NaOH, and N/20-HCl.*
FIG. 4.—*A*. *9-Methyladenine.* *B*. *Barium adenyl pyrophosphate in water at p_H 6·5, in N/20-NaOH, and N/20-HCl.*
FIG. 5.—*A*. *9-Methylhypoxanthine in N/20-NaOH.* *B*. *7-Methylhypoxanthine in N/20-NaOH.*
FIG. 6.—*A*. *9-Methylhypoxanthine in N/20-NaOH.* *B*. *Inosine in N/20-NaOH.*

is insufficient in the present connexion, since the properties of the isomeric 7 (or 9)-derivative in each case are unknown, and since the transposition of the glycosidic linkage from position 7 to 9 (or vice versa) would not in general be expected to cause marked changes in those properties, such as melting points and optical rotations, on which the identifications rest.

Myrbäck, v. Euler, and Hellström (*Z. physiol. Chem.*, 1932, **212**, 12) observed that the ultra-violet absorption spectra of aqueous solutions of adenosine and muscle adenylic acid

have peaks at 2600 A. The p_H values of these solutions must have been different (see below) and it is clear from our results that p_H values may considerably affect the absorption spectra. We have therefore confirmed and extended their results by showing that the spectra of adenylic acid are identical with those of 9-methyladenine (Fig. 3 and Table I). Muscle adenylic acid thus resembles adenosine and 9-methyladenine, and is unlike 7-methyladenine. It is therefore adenine-9-riboside-5-phosphoric acid (III, R = PO_3H_2). This conclusion links these results with the constitutions of various co-enzymes.

The system adenosine triphosphate (adenyl pyrophosphate) ⟷ [adenosine diphosphate] ⟷ adenosine-5-phosphate is recognised as the co-enzyme system of lactic acid formation in voluntary and heart muscles (Meyerhof and Kiessling, *Biochem. Z.*, **1935**, **283**, 83; Lohmann and Schuster, *ibid.*, 1935, **282**, 104). Adenyl pyrophosphate is readily hydrolysed to adenylic acid (Lohmann, *ibid.*, 1931, **233**, 460), and it and adenosine diphosphate are therefore 9-substituted adenines from the results described above. Through the kindness of Dr. Lohmann in presenting us with a sample of barium adenyl pyrophosphate, we have been able to confirm this conclusion by showing that the ultra-violet absorption spectra of this substance closely resemble the spectra of 9-methyladenine (Fig. 4) (compare Myrbäck, v. Euler, and Hellström, *Z. physiol. Chem.*, 1932, **212**, 12). Lohmann (*Biochem. Z.*, 1935, **282**, 120) has already tentatively adopted this formulation on the basis of our earlier communications, although experimental evidence has until now been lacking.

Cozymase, the co-enzyme of alcoholic fermentation, is a derivative of adenosine-5-phosphate (Myrbäck, *Ergeb. Enzymforsch.*, 1933, **2**, 139; *Z. physiol. Chem.*, 1934, **225**, 199; v. Euler, Albers, and Schlenk, *ibid.*, 1935, **237**, 180, 1). Myrbäck, v. Euler, and Hellström (*ibid.*, 1932, **212**, 12) showed that the ultra-violet absorption spectrum of cozymase has its maximum at 2580—2600 A., and these observations indicate that the pentose group is attached to position 9 of the adenine molecule.

The co-enzyme of the lactic acid dehydrogenase of heart muscle (Banga and Szent-György, *ibid.*, 1933, **217**, 39) is an adenine nucleotide, closely related to or identical with cozymase.

Warburg, Christian, and Griese (*Biochem. Z.*, 1935, **282**, 1) showed that the hydrogen-transporting co-enzyme of Warburg's oxidation system is composed of 1 mol. of adenine, 1 mol. of nicotinamide, 3 mols. of phosphoric acid, and 2 mols. of pentose. The assumption that the molecule contains an adenine-pentoside-phosphate group is almost unavoidable. The ultra-violet absorption spectrum has a marked peak at 2600 A., composed of the combined absorptions of the adenine and the nicotinamide residues. Rednction eliminates the absorption due to the pyridine ring, and leaves the peak at 2600 A., now composed solely of the absorption due to the adenine residue. These facts taken in conjunction with our results suggest that the co-enzyme is a derivative of adenine-9-pentoside.

Cocarboxylase (Auhagen, *Biochem. Z.*, 1933, **258**, 330) may also be related to adenylic acid.

Experimental.

Preparation of Materials.—7-Methyladenine was prepared from 2 : 6-dichloro-8-hydroxypurine by methylation (Fischer and Ach, *Ber.*, 1897, **30**, 2208), amination of the resulting 2 : 6-dichloro-8-hydroxy-7-methylpurine, replacement of the 8-hydroxyl by chlorine, and reduction of the chlorine atoms (Fischer, *Ber.*, 1898, **31**, 104).

9-Methyladenine was prepared from 9-methyldichloroadenine (Fischer, *Ber.*, 1897, **30**, 2226).

7-Methylhypoxanthine was obtained by deamination of 7-methyladenine (Fischer, *Ber.*, 1898, **31**, 104), but was more conveniently prepared from theobromine (Fischer, *Ber.*, 1897, **30**, 2400).

9-Methylhypoxanthine was prepared by deamination of 9-methyladenine (Fischer, *Ber.*, 1898, **31**, 104).

Adenosine was prepared from the hydrolysis products of yeast nucleic acid by processes which differed but slightly from those of Levene (" Nucleic Acids," 1931, Chemical Catalog Co., New York). After being dried at 110° over phosphoric oxide, it melted at 230° (Found : C, 45·2; H, 5·0; N, 26·3; amino-N, 5·1. Calc. for $C_{10}H_{13}O_4N_5$: C, 45·0; H, 4·9; N, 26·2; amino-N, 5·0%).

Inosine was prepared by deamination of adenosine with barium nitrite and acetic acid

(Levene and Tipson, *J. Biol. Chem.*, 1935, **111**, 313). In this preparation, deamination proceeds at room temperature for 3 days, to be followed by crystallisation of the inosine when the solution is cooled. It is our experience that barium nitrate, formed by aerial oxidation of the nitrous acid, separates in characteristic prisms during the deamination period and that this is not avoided by using boiled solutions and filling the loosely-corked vessel with nitrogen at the beginning of the reaction. The aqueous solution must be decanted from the barium nitrate before the inosine is allowed to separate. Mention is made of these facts, because we were at first led astray by obtaining with the barium nitrate precipitate the characteristic purple-red colour of the phloroglucinol-hydrochloric acid test for pentoses (Tollens). The colour is formed by the nitrate ion, however, and the coloured material does not give the characteristic absorption band given by pentoses in this test, although it is extracted by amyl alcohol. This is also the behaviour of galactose. In the orcinol-hydrochloric acid test (Bial), nitrates give a brown coloration, ultimately red-brown, which might be confused with that given by fructose, and thus differ from pentoses, which give a greenish-blue colour.

Inosine was obtained in needles, m. p. 218° after being dried at 110° in a vacuum over phosphoric oxide (Found : C, 44·3; H, 4·5; N, 20·7; amino-N, 0·1. Calc. for $C_{10}H_{12}O_5N_4$: C, 44·8; H, 4·5; N, 20·9; amino-N, 0%). The estimation of amino-nitrogen was carried out for 1 hour at room temperature in a van Slyke micro-apparatus; Wilson (*J. Biol. Chem.*, 1923, **56**, 183) states that inosine shows a trace of amino-nitrogen under these conditions.

The carbon and hydrogen estimations were carried out by Dr. Ing. A. Schoeller, and we are indebted to Dr. T. F. Macrae for the estimations of nitrogen by the micro-Kjeldahl method. In analysing purine compounds by this method, it is necessary to oxidise for 2½ hours to convert all the nitrogen into ammonia.

Spectrographic Data.—Measurements were made with a Hilger medium quartz spectrograph and Spekker photometer. The light source was a condensed spark between tungsten-steel electrodes.

Samples were anhydrous, having been dried in a vacuum at 110° over phosphoric oxide, but the barium adenylpyrophosphate was the hexahydrate. Solutions were made to a strength of *M*/5000 and were examined immediately in a layer thickness of 1 cm. against controls.

TABLE I.

	λ, A.		$\epsilon \times 10^4$.	
	N/20-HCl.	*N*/20-NaOH.	*N*/20-HCl.	*N*/20-NaOH.
Adenine	2600	2580	1·32	1·36
7-Methyladenine	2690	2690	1·46	1·14
9-Methyladenine	2600	2600	1·42	1·47
Adenosine	2600	2600	1·42	1·43
Hypoxanthine	2480	2620	0·96	1·00
7-Methylhypoxanthine	2500	2610	0·98	1·01
9-Methylhypoxanthine	2480	2550	1·03	1·21
Inosine	2470	2540	1·32	1·34
Muscle adenylic acid	2600	2600	1·29	1·40
Adenyl pyrophosphate	2600	2600	1·49	1·38

Conversion of Muscle Adenylic Acid into Adenosine by Bone Phosphatase.—A solution of muscle adenylic acid (485 mg., equivalent theoretically to 43·3 mg. of phosphorus) in water (25 c.c.) and a little 2*N*-sodium hydroxide was mixed with bone phosphatase (100 mg; A/W 0·23) in water (10 c.c.). The mixture was adjusted to p_H 8·6 with sodium hydroxide, diluted to 50 c.c., and incubated for 20 hours at 37° after the addition of a little chloroform.

Time, hrs.	0	20
Total P, mg.	42·6	43·2
Free P, mg.	0·2	44·0

The solution was brought to p_H 4·4 with acetic acid, heated at 100° for 4 minutes, and centrifuged. Phosphate ions were removed by addition of a slight excess of baryta and filtration, and the clear colourless solution was freed exactly from barium by means of sulphuric acid, rhodizonic acid being used as indicator. The resulting solution was concentrated under reduced pressure and cooled. The fine colourless needles which separated in good yield were recrystallised from water, and after being dried at 110° in a vacuum over phosphoric oxide melted at 230° alone or when mixed with authentic adenosine, m. p. 230°, prepared from yeast nucleic acid and having the same crystalline appearance. $[\alpha]_D^{20°}$ in 5% sodium hydroxide solution was − 68·2° (*c* 4·12); Levene (*J. Biol. Chem.*, 1920, **41**, 492) gives − 68·5°.

The picrate of the material under examination, prepared in aqueous solution, formed yellow leaflets, sintering at 195° and melting at 198°. The picrate of authentic adenosine (*ex* yeast nucleic acid) crystallised in the same form and also sintered at 195° and melted at 198°. Levene and Jacobs (*Ber.*, 1909, **42**, 2703) state that the picrate sinters at 180° and is molten at 185° (corr.).

The palladochloride of adenosine (Gulland and Macrae, J., 1932, 2231) is not characteristic, consisting of minute yellow granules coalescing in clusters. The palladochlorides of the two substances under consideration were identical in appearance.

This comparison of physical properties indicates that the adenosine prepared by dephosphorylation of muscle adenylic acid is identical with that prepared from yeast nucleic acid.

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[*Received, April 7th*, 1936.]

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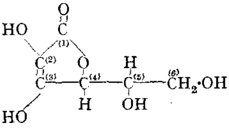
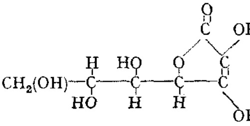
177. *The Crystalline Structure of the Sugars. Part III. Ascorbic Acid and Related Compounds.*

By E. G. COX and T. H. GOODWIN.

PRELIMINARY *X*-ray and optical measurements (Cox, *Nature*, 1932, **130**, 205) were employed extensively in the elucidation of the structure of the "hexuronic acid" which Szent-Gyorgyi (*Biochem. J.*, 1928, **22**, 1387; *Nature*, 1932, **129**, 576) identified with the antiscorbutic factor, vitamin-*C*, now known as ascorbic acid, but it was considered advisable to defer detailed investigation until the constitution had been definitely established (Herbert, Hirst, Percival, Reynolds, and Smith, J., 1933, 1270). The present paper contains an account of the *X*-ray analysis of this compound (I), together with data for a number of related compounds, *viz.*, 2 : 3-dimethyl ascorbic acid, galacto-ascorbic acid monohydrate (II), imino-galacto-ascorbic acid (III), and 2 : 3-dimethyl gluco-ascorbic acid (IV).

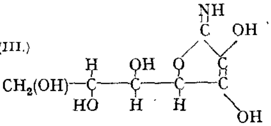
(I.)

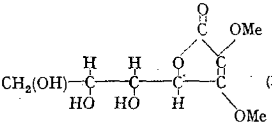




(II.)

(III.)





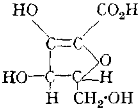
(IV.)

Ascorbic acid crystallises in the monoclinic system with four molecules of $C_6H_8O_6$ in the unit cell, the space group being $P2_1$, which is characterised by a two-fold screw axis parallel to the *b*-axis of the crystal. For this space group two asymmetric units per elementary cell are required, so that in this compound two molecules must be associated together in one asymmetric unit. There is no means of determining the relationship between these two molecules, except by intensity measurements, but the existence of an almost perfect halving of the {*hk*0} planes when *h* is odd strongly suggests that they are connected by a pseudo-glide plane of symmetry perpendicular to the *c*-axis. (The above-mentioned halvings might, indeed, be due to some distribution of scattering matter not involving any pseudo-symmetry, but the assumption of this additional element of symmetry is the more reasonable and is justified by the results). Since the substance is optically active, there cannot be *d*- and *l*-molecules present, and hence the molecules themselves

presumably possess a plane of symmetry, and lie in the cell so that this plane of symmetry either contains the *c*-axis or is perpendicular to it. (The existence of the pseudo-plane of symmetry is not inconsistent with the presence of an asymmetric carbon atom, since the efficiencies of carbon and oxygen for the scattering of *X*-rays are nearly the same and the hydrogen atoms may be neglected; thus, in the molecule a carbon atom may have for its "mirror image" either an oxygen atom or a hydroxyl group.)

Now, the crystals have a negative birefringence which is much higher than in any other sugar derivative so far studied. This suggests a molecule in which most of the atoms lie in one plane, this plane being perpendicular to the *b*-axis, since the latter is the direction of the minimum refractive index. In support of this, it is found that the intensities of the {020} reflections fall off regularly, the structure factors being roughly constant for the first three orders, as would be expected for a molecule in which most of the atoms lie in the {020} planes (see Table II).

If the molecule were quite flat, the first case mentioned above, *i.e.*, the *c*-axis in the plane symmetry of the molecule, would be possible, but construction of a model of formula (I) shows that the molecule, although relatively flat, is not sufficiently so to give rise to the observed pseudo halvings. (The strongest $\{2n+1, k, 0\}$ plane observed has a structure factor less than one-tenth of the lowest recorded in Table I.) Consequently, the plane of symmetry must be perpendicular to the plane of the ring. These considerations, as pointed out by Cox and Hirst (*Nature*, **1933**, **131**, 402), rule out the furancarboxylic acid structure at one time advocated by Micheel and Kraft (*ibid.*, p. 274), and also adopted by Reichstein, Grüssner, and Oppenauer in describing their synthesis of *d*-ascorbic acid (*Helv. Chim. Acta*, **1933**, **16**, 561). Although the approximate equality of carbon and oxygen for the scattering of *X*-rays may be assumed, this molecule (V) cannot have a plane of symmetry either in or perpendicular to the plane of the ring.



(V.)

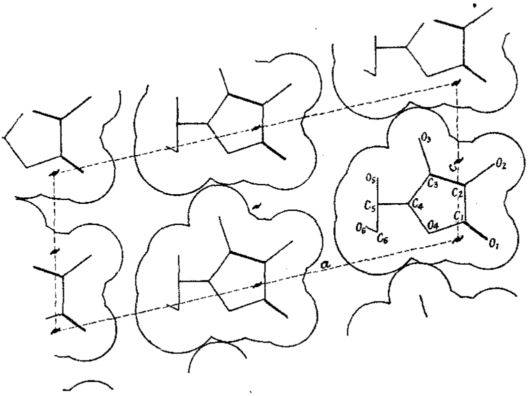
In a similar way, the enolic form of 3-ketogulopyranolactone (the pyranose molecule corresponding to ascorbic acid) cannot have a plane of symmetry either in or perpendicular to the mean plane of the ring, and is not sufficiently flat to account for the observed {020} structure factors. Ascorbic acid cannot, therefore, be a pyranose compound.

The constitution (I) established by Hirst and co-workers (*loc. cit.*), on the other hand, is not open to this objection, and if the side-chain atoms are disposed as in the figure, there is almost a plane of symmetry perpendicular to the plane of the ring, passing through C_4 and C_5 and bisecting the C_1C_2 bond. In this model C_3 and O_5 are assumed to be equivalent to O_4 and C_6 respectively, and are equidistant from the pseudo-plane of symmetry; O_3 and O_6 are also approximately equivalent.

The foregoing considerations thus lead to the conclusion that the molecules are arranged in the (020) planes with their C_1C_2 bonds parallel to the *c*-axis. It remains, therefore, to determine the positions of the four molecules in the unit cell and of the twelve atoms in each molecule. In theory, this can be done, without any assumptions as to the interatomic distances, by means of a sufficiently large number of measurements of reflection intensities, but in this case, the evaluation of 39 parameters is necessary even if the pseudo-glide plane is treated as a genuine one. (Corresponding atoms in the two molecules connected by the glide plane must have the same parameters parallel to the *b*-axis.) The crystallographic importance of ascorbic acid, however, is not sufficient to justify the labour involved, and it is more convenient to determine the molecular positions using a model such as that shown in the figure. The parameters are thus reduced to three, *viz.*, two, u_1 and w_1, fixing the position of the screw axis with respect to a reference atom in the standard molecule, and one, w_2, giving the distance of the glide plane from the same atom.

Having regard to the uncertainty as to the divergence of the valency angles in the ring from $109\frac{1}{2}°$, the simplest assumption has been made in constructing the model, *viz.*, that the ring is a regular pentagon, the angles of which are 108°, and the sides C–C and C–O are equal to 1·50 A. Outside the ring the tetrahedral angle has been maintained, and the distances C—C = 1·54 A., C—O = 1·46 A., and C=O = 1·15 A. have been adopted.

As pointed out in the earlier papers of this series (J., 1935, 978, 1495), the properties of the sugars and similar compounds suggest the occurrence of extensive association between hydroxyl groups; we have therefore assumed that the minimum distance between the oxygen atoms of hydroxyl groups is 2·5 A. in accordance with recent measurements (*e.g.*, Zachariasen, *J. Chem. Physics*, 1935, 3, 158; Bernal and Megaw, *Proc. Roy. Soc.*, *A*, 1935, 151, 384). To determine whether a given arrangement of molecules is satisfactory from the point of view of space filling, it has been found advantageous to use actual models (scale 2 cm. = 1 A.) in which the hydroxyl groups are represented by spheres of radius 2·5 cm., these spheres being cut away on one side so that the correct C—O distance of 2·9 cm. can be maintained. The carbon and oxygen atoms are represented by spheres of radius 1·5 cm. The use of these large spheres to represent hydroxyl groups enables the models to be packed together with these spheres in contact, thus ensuring that the correct minimum O—O distance is attained. (In a similar way spheres of radius 3·7 cm. may be used to represent methyl groups when necessary.) Molecular arrangements involving too close approach of atoms in neighbouring molecules are readily detected in this way, and can be



eliminated from consideration. These models are also useful for the rapid approximate calculation of structure factors; for this purpose they are arranged in the appropriate positions and a shadow projected, by means of a beam of parallel light, on to a sheet of photographic paper, from which, after development, the atomic co-ordinates can be measured.

The structure factor F_{hkl} for any plane (hkl) having glancing angle θ is given by

$$F_{hkl} = \Sigma f_\theta e^{2\pi i(hx/a + ky/b + lz/c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f_θ (see p. 773) is the atomic scattering factor of the atom situated at (x, y, z), summation being made over one complete unit cell. The values of F for any structure may then be compared with those derived from the experimental intensities (I_{hkl}) by means of the formula

$$F_{hkl} = \text{const.} \times I_{hkl}^{\frac{1}{2}} \,.\, L_\theta^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $L_\theta = (1 + \cos^2 2\theta)/\sin 2\theta$.

For $\{h0l\}$ planes, (1) reduces to $F_{h0l} = \Sigma f_\theta \,.\, \cos 2\pi(hx/a + lz/c)$ when the origin is taken at the intersection of the screw axis with the (010) plane.

Structure factors were calculated for the various planes by means of (1), all possible values

of the three parameters u_1, w_1, and w_2 being taken and compared with the experimental values deduced from (2). Only one combination of parameters gave reasonable agreement, and this was also found to be satisfactory from the point of view of space-filling. The molecular arrangement so obtained is shown in the figure, and the comparison of the structure factors $F_{theo.}$ and $F_{exp.}$ deduced from this structure and from the experimental data respectively is recorded in Table I for the (h00) planes and in Table II for the (0k0) and (00l) planes. In these tables, (200) and (020) are taken as standards, and the arbitrary scale of intensity has been adjusted in each table so that $F_{theo.} = F_{exp.}$ for (200) and (020) respectively. The agreement between calculated and observed factors is satisfactory in view of the approximations made, and indicates that the molecular model adopted is substantially correct. (Various modifications of the model which have been made do not lead to any improvement in the agreement between theoretical and experimental structure factors.)

TABLE I.

hkl.	$f_{\theta C}$.	$f_{\theta O}$.	I_{hkl}.	L_θ.	$F_{theo.}$.	$F_{exp.}$.	hkl.	$f_{\theta C}$.	$f_{\theta O}$.	I_{hkl}.	L_θ.	$F_{theo.}$.	$F_{exp.}$.
200	5·37	7·74	100	10·8	33·8	34	800	2·57	4·74	5	2·2	40·3	16
400	4·22	6·80	1	5·2	3·2	5	1000	2·16	3·90	25	1·6	60·0	44
600	3·18	5·75	10	3·2	56·0	20							

TABLE II.

020	3·55	6·16	100	3·8	118 *	118	003	2·56	4·75	0·1	2·2	4·7	5
040	2·08	3·68	20	1·4	119	80	004	2·05	3·60	1	1·4	12·0	19
060	1·72	2·40	10	1·0	79·5	86	220	3·16	5·95	50	3·6	89·7	86
001	4·98	7·44	10	8·0	23·9	28	230	2·55	4·65	2	2·2	15·1	22
002	3·49	6·09	0·14	3·8	4·7	5	$10\bar{1}$	5·02	7·48	8	8·4	28·0	21

* For a completely flat molecule F_{020} (theo.) would be 233.

Table III gives the atomic co-ordinates for a single molecule referred to the principal axes of the cell, the origin being situated at the intersection of one of the screw axes and the plane of the molecules. If the co-ordinates of a reference atom in one molecule are (u, v, w,) then the corresponding atom in the molecule which is derived from the first by the operation of the glide plane has co-ordinates (u + 0·500, v, w + 0·814), and that in the molecule derived from the first by the action of the screw axis ($-$ u, v + 0·500, $-$ w).

TABLE III.

Atom.	u.	v.	w.	Atom.	u.	v.	w.	Atom.	u.	v.	w.
C_1	0·982	0	0·106	C_3	0·068	0	0·471	C_5	0·197	0·140	0·349
O_1	0·925	0	0·976	O_3	0 095	0	0·707	O_5	0·197	0·268	0·517
C_2	0·982	0	0·349	C_4	0·121	0	0·309	C_6	0·197	0·280	0·171
O_2	0·908	0	0·455	O_4	0·068	0	0·090	O_6	0·225	0·405	0·219

The figure is a projection on (010) of two of the four molecules in the unit cell, the other two, derived from these by the screw axis, being $\frac{1}{2}b$ above. It will be seen that the molecules connected by the pseudo-glide plane are oriented so that their side chains are all in the same direction (*above* the plane of the C_4O rings) and not alternately in opposite directions; the latter arrangement would be consistent with the symmetry requirements but not with the intensities of (220) and (230). Since $\frac{1}{2}b$ is only 3·16 A. and the molecules are not completely planar, the side-chain atoms in any layer penetrate somewhat into the next layer; this accounts for the apparent gaps between the molecules in the figure. It is noteworthy that the distance between the completely flat parts of the molecules in successive layers, *i.e.*, 3·16 A., is identical with that found in maleic acid (Yardley, J., 1925, **127**, 2207). It thus appears that the carbon–carbon distance in unsaturated aliphatic compounds may be appreciably less than in aromatic substances, for the latter distance is never less than 3·4 A.

In addition, a hydrogen or hydroxyl bond appears to exist between the ring oxygen atom of one molecule and the O_3 atom of the next, the separation of these atoms being about 2·5 A. Since the former behaves neither as a true ether nor as a true lactone oxygen, this cannot be taken as evidence that similar bonds exist with ethers or lactones in general.

It should be noted finally that both *d*- and *l*-synthetic ascorbic acids have been examined

and found to be completely identical in optical properties (except rotatory power) and crystalline structure with the natural *l*-compound obtained from plant and animal sources.

Of the other compounds examined, galacto-ascorbic acid monohydrate has been studied most fully. The presence of an additional asymmetric carbon atom in the molecule, and of water of crystallisation, together with the technical difficulties peculiar to the triclinic system, have precluded a very detailed investigation, but the optical properties and cell dimensions show that the molecule is somewhat similar to that of ascorbic acid and have enabled its orientation in the unit cell to be determined (see p. 774).

Experimental.

f-*Values.*—For the calculation of theoretical structure factors (F), James and Brindley's table of atomic scattering factors (f) (" Internationale Tabellen zur Bestimmung von Kristallstrukturen, 1935, p. 571; *Z. Krist.*, 1931, **78**, 470) is in general use. Their data, however, are tabulated for intervals of 0·1 in $(\sin \theta)/\lambda$, so that for the copper-$K\alpha$ radiation employed in this series of researches the maximum value of $(\sin \theta)/\lambda$ is 0·65 and only seven points can be used to determine the form of the f-curve. Moreover, with organic crystals small values ($<0·2$) of $(\sin \theta)/\lambda$ are common, and in this region interpolation is less certain than for higher values. We have therefore calculated the f-values for neutral carbon and neutral oxygen for increments of 0·01 in $(\sin \theta)/\lambda$ by the method of James and Brindley from data given by them (*Phil. Mag.*, 1931, **12**, 81, Tables I, II, and III). For carbon, the following values of the screening constants (s) were used: (1,0) electrons, $s = 0·36$; (2,0) electrons, $s = 2·6$; (2,1) electrons, $s = 4·1$. The f-values are shown in Table IV as functions of $(\sin \theta)/\lambda$, and in Table V as functions of d, the lattice spacing. No temperature factor has been applied to the results.

Table IV.

$(\sin \theta)/\lambda$.	f_C.	f_O.	$(\sin \theta)/\lambda$.	f_C.	f_O.	$(\sin \theta)/\lambda$.	f_O.	f_O.	$(\sin \theta)/\lambda$.	f_C.	f_O.
0	6·00	8·00	0·18	3·23	5·75	0·36	1·89	3·24	0·54	1·63	2·07
0·01	5·99	8·00	0·19	3·05	5·59	0·37	1·86	3·14	0·55	1·61	2·05
0·02	5·95	7·98	0·20	2·97	5·42	0·38	1·83	3·05	0·56	1·60	2·01
0·03	5·84	7·95	0·21	2·87	5·23	0·39	1·81	2·96	0·57	1·59	1·99
0·04	5·71	7·89	0·22	2·76	5·08	0·40	1·80	2·87	0·58	1·58	1·96
0·05	5·58	7·83	0·23	2·66	4·91	0·41	1·78	2·80	0·59	1·56	1·94
0·06	5·38	7·74	0·24	2·58	4·75	0·42	1·77	2·72	0·60	1·55	1·91
0·07	5·20	7·61	0·25	2·50	4·61	0·43	1·75	2·64	0·61	1·54	1·89
0·08	5·00	7·46	0·26	2·42	4·46	0·44	1·74	2·57	0·62	1·53	1·87
0·09	4·80	7·31	0·27	2·35	4·32	0·45	1·73	2·52	0·63	1·51	1·84
0·10	4·60	7·20	0·28	2·28	4·18	0·46	1·72	2·48	0·64	1·50	1·83
0·11	4·40	7·00	0·29	2·21	4·04	0·47	1·71	2·42	0·65	1·49	1·81
0·12	4·21	6·80	0·30	2·16	3·90	0·48	1·70	2·36	0·66	1·47	1·80
0·13	4·04	6·64	0·31	2·11	3·77	0·49	1·68	2·30	0·67	1·45	1·78
0·14	3·85	6·47	0·32	2·05	3·65	0·50	1·67	2·25	0·68	1·44	1·76
0·15	3·69	6·29	0·33	2·01	3·54	0·51	1·66	2·21	0·69	1·42	1·75
0·16	3·53	6·11	0·34	1·96	3·43	0·52	1·65	2·17	0·70	1·40	1·74
0·17	3·37	5·93	0·35	1·93	3·34	0·53	1·64	2·12			

Table V.

d.	f_C.	f_O.	d.	f_C.	f_O.	d.	f_C.	f_O.	d.	f_O.	f_O.
0·7	1·37	1·73	1·9	2·39	4·43	3·0	3·41	6·00	5·5	4·79	7·31
0·8	1·53	1·86	2·0	2·50	4·61	3·2	3·59	6·19	6·0	4·94	7·42
0·9	1·61	2·04	2·1	2·60	4·81	3·4	3·73	6·35	7·0	5·16	7·60
1·0	1·67	2·23	2·2	2·69	4·99	3·6	3·87	6·49	8·0	5·33	7·72
1·1	1·74	2·50	2·3	2·78	5·13	3·8	4·00	6·61	9·0	5·46	7·78
1·2	1·79	2·75	2·4	2·87	5·29	4·0	4·13	6·73	10·0	5·57	7·83
1·3	1·83	3·00	2·5	2·96	5·43	4·2	4·25	6·84	12·0	5·68	7·89
1·4	1·90	3·25	2·6	3·05	5·56	4·4	4·35	6·94	14·0	5·76	7·91
1·5	1·99	3·50	2·7	3·14	5·67	4·6	4·44	7·03	16·0	5·82	7·93
1·6	2·09	3·75	2·8	3·23	5·79	4·8	4·51	7·11	20·0	5·89	7·95
1·7	2·19	4·00	2·9	3·31	5·90	5·0	4·60	7·20	50·0	5·99	8·00
1·8	2·29	4·23									

These values are not strictly reliable for a substance such as ascorbic acid containing several doubly bound atoms, but are probably sufficiently accurate in view of the other approximations which must necessarily be made at this stage in the analysis of the compound.

l-*Ascorbic Acid* (I).—For the earlier work, portions of the same samples used to establish

the constitution (Hirst and co-workers, *loc. cit.*) were employed; these had been prepared from adrenal glands and from paprica. Later *X*-ray and optical measurements confirmed that the synthetic *l*-ascorbic acid is identical with the natural product, and that the synthetic *d*-acid is also indistinguishable from it except in rotatory power. Crystallisation from several solvents and under a variety of conditions gave no indication of dimorphism; characteristic square or slightly elongated crystals, similar to those originally described by Szent-Gyorgyi (*Biochem. J.*, 1928, **22**, 1408, Fig. 2a) were invariably obtained. These are monoclinic, tabular on *a* {100}, and exhibit the forms *r* {101}, *s* {201}, and *p* {210}. The approximate equality of the angles *a* : *r* (59°) and *a* : *s* (61°) gives the crystals a pseudo-orthorhombic habit, which supports the view that the additional *X*-ray halvings which are observed are due to a pseudo-plane of symmetry perpendicular to the *c*-axis.

The cell dimensions are $a = 16{\cdot}95$, $b = 6{\cdot}32$, $c = 6{\cdot}38$ A., and $\beta = 102\frac{1}{2}°$. The number (n) of molecules in the unit cell is four; d (calc.) = 1·74 g./c.c. (obs. = 1·74). Oscillation photographs show that {010} is halved, and that all {*hk*0} planes for which *h* is odd are either absent or exceedingly weak. The space group is therefore $P2_1$ (C_2^2); the significance of the {*hk*0} halvings has been discussed on p. 769. The intensities of the various reflections recorded in Tables I and II were measured on an arbitrary scale by photographic comparison, a strong reflection being reduced in a known ratio by means of aluminium absorbing screens until equal to a weaker one as judged by eye. Since the best available crystals were quite small, these measurements are probably not accurate to more than 10—20%.

The refractive indices, determined by immersion methods, are $\alpha = 1{\cdot}476 \pm 0{\cdot}002$, $\beta = 1{\cdot}594 \pm 0{\cdot}002$, and $\gamma = 1{\cdot}750 \pm 0{\cdot}005$. (All refractive indices recorded in this paper are for the sodium-*D* wave-length.) γ is the acute bisectrix (*i.e.*, the crystals are optically positive) and α is parallel to [*b*]. The plane of the optic axes is perpendicular to (010) and inclined at 42° ± 2° to (100). Owing to the difficulty of distinguishing between *r* and *s*, it was not determined whether the above angle is in the acute or the obtuse angle β. The above refractive indices may be compared with the values $\alpha = 1{\cdot}465$, $\beta = 1{\cdot}600$, and $\gamma = 1{\cdot}747$ for $\lambda = 5461$ A. given by Hendricks (*Nature*, 1934, **133**, 178).

It is of interest to note that the mean molecular refractivity of crystalline ascorbic acid, calculated for sodium light by the Lorentz–Lorenz equation, is 34·7, which is in good agreement with the theoretical value 35·0. On the other hand, the theoretical value for the ketonic forms of ascorbic acid would be 33·9.

d-*Galacto-ascorbic Acid Monohydrate* (II).—This compound (Baird, Haworth, Herbert, Hirst, Smith, and Stacey, J., 1934, 65) crystallises from water in large but rather poor triclinic asymmetric crystals. The best crystal measured exhibited the forms *a* {100}, *a′* {$\bar{1}$00}, *b* {010}, *b′* {0$\bar{1}$0}, *c* {001}, *c′* {00$\bar{1}$}, *m* {110}, and *p′* {0$\bar{1}$1}. Goniometric measurements were made to identify the above faces, but were not sufficiently accurate for the calculation of reliable axial ratios. Actually, a number of interfacial angles was measured with an accuracy of ¼° by means of series of Laue photographs, each series consisting of several exposures in which the angular setting of the crystal differed by successive ½° intervals. In some cases more accurate values were obtained by means of the ionisation spectrometer. The lengths of the various axes were determined from rotation photographs, and the primitive cell deduced from them was confirmed by the spectrometer measurements and by oscillations about the *b*- and *c*-axes.

The cell dimensions are $a = 5{\cdot}96$, $b = 8{\cdot}56$, $c = 4{\cdot}75$ A. (whence $a : b : c = 0{\cdot}6966 : 1 : 0{\cdot}5551$), $\alpha = 91° 48'$, $\beta = 102° 23'$, and $\gamma = 79° 06'$; $n = 1$; d (calc.) = 1·60 g./c.c. (obs. = 1·60). Space group $P1$ (C_1^1). The principal interfacial angles measured on the ionisation spectrometer are *a* (100) : *b* (010) = 100° 45½′, *b* (010) : *c* (001) = 90° 33′, *c* (001) : *a* (100) = 77° 44½′, and *a* (100) : *q* (1$\bar{1}$0) = 30° 40½′ (calc. = 30° 39½′).

The refractive indices are $\alpha = 1{\cdot}46$, $\beta = 1{\cdot}57$, and $\gamma = 1{\cdot}68$. The minimum refractive index, α, is inclined at 30° ± 5° to the normal to *c* (001) and at 74° ± 5° to the normal to *b′* (0$\bar{1}$0). Assuming that the mean plane of the molecule is perpendicular to α, the molecular " thickness " is about 3·6 A.

d-*Imino-galacto-ascorbic Acid* (III).—Large crystals of this compound (Haworth, Hirst, Jones, and Smith, J., 1934, 1197) were available, but all were found to be twinned. They are apparently orthorhombic pseudo-tetragonal combinations of *p* {104}, *q* {014}, and *c* {001}, fully developed and twinned on *m* {110}, which occasionally appears as a partially developed form. The lines of junction of the individual crystals in a twin are visible on *c* {001}, but they are not parallel to any simple crystallographic axes.

Through *c* {001} can be seen in convergent polarised light a centred acute bisectrix figure which turns through 90° when one of the above-mentioned junction lines is crossed. The sign

is positive, the refractive indices being $\alpha = \beta = 1{\cdot}623 \pm 0{\cdot}002$, $\gamma = 1{\cdot}64$ ($\beta - \alpha = 0{\cdot}001$). The optic axial angle is $2E = 47°$, and there is strong dispersion of the optic axes ($\rho > \upsilon$).

Goniometric measurements gave the following results:

	Obs.	Calc.
c (001) : p (104) =	55° 16′	—
c (001) : q (014) =	55 10	—
p (104) : q (014) =	70 36	71° 00′
q (014) : m (110) =	*ca.* 55	54 30

The difference between $c : p$ and $c : q$ is probably not significant; if both are assumed to be equal to 55° 13′ the axial ratios are $a : b : c = 1{\cdot}000 : 1 : 5{\cdot}758$.

X-Ray rotation photographs about the *a* and *b* axes are indistinguishable; the cell dimensions are $a = b = 6{\cdot}7$, $c = 38{\cdot}5$ A., whence $a : b : c = 1{\cdot}00 : 1 : 5{\cdot}74$ (cf. goniometric values above); $n = 8$; d (calc.) $= 1{\cdot}58$ g./c.c. (obs. 1·58). In view of the large number of molecules in the unit cell and the difficulties caused by twinning, the importance of the substance did not appear sufficient to warrant further investigation.

Dimethyl d-*Gluco-ascorbic Acid* (IV).—Fairly good, but very small crystals of this compound {m. p. 94°, $[\alpha]_D = -22°$ in water (c, 4·0)} were supplied by Mr. J. K. N. Jones of this laboratory. They are elongated monoclinic combinations of *a* {100} and *R* {10$\bar{1}$}, terminated by *m* {011}. The cell dimensions are $a = 9{\cdot}66$, $b = 7{\cdot}70$, $c = 8{\cdot}77$, and [102] = 15·89 A., whence $\beta = 115° 59'$ and $a : b : c = 1{\cdot}254 : 1 : 1{\cdot}139$; $n = 2$; d (calc.) $= 1{\cdot}43$ g./c.c. (obs. 1·45). The space group is $P2_1$ (C_2^2). The refractive indices are $\alpha = 1{\cdot}46$ (parallel to the *b*-axis) and $\gamma = 1{\cdot}60$. These data suggest that the molecules are relatively flat and lie in the (020) planes (thickness $\frac{1}{2}b$, *i.e.*, 3·85 A.).

SUMMARY.

A crystallographic examination of ascorbic acid has been made, and a structure which is in good accord with the optical properties and *X*-ray reflection intensities is proposed. In connection with this and similar work it has been considered advisable to calculate atomic scattering factors for carbon and oxygen for smaller intervals of $(\sin\theta)/\lambda$ than those normally available: tables of *f* for intervals of 0·01 in $(\sin\theta)/\lambda$ are given in the experimental part of the paper. *X*-Ray data are also recorded for some substances related to ascorbic acid.

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178. *The Stereochemistry of Quadricovalent Atoms: Copper and Silver.*

By E. G. COX, W. WARDLAW, and K. C. WEBSTER.

EARLIER work (*e.g.*, Cox, Wardlaw, and Webster, J., 1935, 1475; Cox and Webster, *ibid.*, p. 731; Cox, Sharratt, Wardlaw, and Webster, this vol., p. 129) has shown that many quadricovalent complexes of *bivalent* platinum, palladium, nickel, and copper possess a planar configuration, and that this configuration is maintained even when considerable changes are made in the nature of the co-ordinated groups. On the other hand, it appears that a change in the principal valency of the metal leads to a change in the spatial distribution of its bonds, since trimethylplatinic chloride (Cox and Webster, *Z. Krist.*, 1935, **90**, 561) and nickel carbonyl (Brockway and Cross, *J. Chem. Physics*, 1935, **3**, 828) both possess a tetrahedral configuration. We have further investigated the dependence of configuration on valency, and it is now shown that, in sharp contrast to the planar derivatives of bivalent copper, the four attached groups in quadricovalent cuprous complexes are disposed tetrahedrally about the metal atom; similarly, silver is found to be planar when bivalent and tetrahedral when univalent.

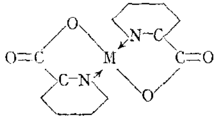
Anhydrous quadricovalent derivatives of bivalent silver suitable for *X*-ray studies are

difficult to prepare; we have found, however, that the argentic derivative of picolinic acid (I) possesses a planar configuration. This result is based on the high birefringence of the compound, and on its isomorphism with the corresponding copper derivative. The birefringence (> 0·26) shows that the two picolinic acid residues in each complex must be coplanar (or very nearly so); with a tetrahedral distribution of the silver bonds the two picolinic acid groups would lie in two planes at right angles, and the birefringence would be very low. The crystals of both the copper and the silver derivative are too small for single-crystal *X*-ray examination, but the isomorphism has been established by microscopic investigation and by *X*-ray powder photographs. The results of the latter are given in Table I, where the principal spacings (*d*) and the corresponding approximate intensities (*I*) are given for each substance.

TABLE I.

Silver picolinate.				Copper picolinate.			
d (A.).	*I*.	*d* (A.).	*I*.	*d* (A.).	*I*.	*d* (A.).	*I*.
8·57	m.	2·43	m.	8·46	m.	2·42	m.
6·73	v.s.	2·32	m.	7·01	v.s.	2·32	m.w.
—	—	2·23	m.	4·79	m.w.	2·23	m.
4·28	m.	2·08	w.	4·31	s.	—	—
3·96	m.s.	1·97	m.w.	—	—	1·96	m.w.
3·70	m.s.	1·86	m.s.	3·79	s.	1·89	m.w.
3·29	v.w.	1·75	m.w.	3·27	m.w.	1·76	v.w.
3·20	v.s.	1·68	w.	3·20	v.s.	1·70	v.w.
3·09	m.	1·60	m.w.	—	—	1·60	m.
2·86	w.	1·54	v.w.	—	—	—	—
2·73	w.	1·49	w.	—	—	1·49	v.w.
2·57	m.			2·57	m.s.		

The configuration of the copper compound has been determined by an *X*-ray examination of single crystals of the dihydrate, in which the quadricovalent complex is found definitely to have a planar *trans*-structure. Both the *X*-ray data and the readiness with which the hydrate loses water to form the anhydrous compound indicate that the water molecules in the former are not co-ordinated to the copper atom, and that therefore the complex has the same configuration (*i.e.*, planar *trans*) in the anhydrous salt as in the hydrate. This is confirmed by the similarity of the optical data, both forms having very high birefringence.

(I.) 

$$\left[Cu \leftarrow \left(S{=}C{<}^{CH_3}_{NH_2} \right)_4 \right]Cl \quad (II.)$$

It is noteworthy that a second form of copper picolinate, having different crystalline structure and chemical properties, may be obtained by using alcoholic solutions in the preparation; detailed examination was not feasible on account of the microcrystalline nature of this form, but the high birefringence suggests a planar structure, and it is possible that this form is the *cis*-isomeride, since polymerisation is highly improbable.

In sharp contrast to the planar bivalent compounds, we find that quadricovalent argentous and cuprous derivatives possess a tetrahedral distribution of valencies. The only previous evidence on the configuration of compounds of this type has been that of Hein and Regler, who in a preliminary note (*Naturwiss.*, 1935, **23**, 320) claimed to have effected a partial resolution of an argentous derivative of 8-hydroxyquinoline, but full details have not yet been published. In the present paper the results are given of detailed *X*-ray studies of potassium cuprocyanide, $K_3[Cu(CN)_4]$, tetrakisthioacetamide-cuprous chloride (II), and ***tetrakisthioacetamide-argentous chloride.*** In each of these compounds a tetrahedral valency distribution has been found.

Potassium cuprocyanide forms large rhombohedral crystals which, in view of their strong pyroelectric properties and the absence of vertical planes of symmetry (as shown

by Laue photographs), must be assigned to the trapezohedral class (D_3). *X*-Ray examination shows that there are two molecules in the rhombohedral unit cell, so that each complex ion $[Cu(CN)_4]$ possesses three-fold axial symmetry. This indicates a tetrahedral disposition of the Cu–CN bonds, one being parallel to the trigonal axis. The low birefringence is in agreement with the tetrahedral arrangement. Since the crystals are somewhat unstable, no attempt has been made to fix atomic positions, but the absence or weakness of the odd orders of {100} and {111} suggests a pseudo-body-centred arrangement of the copper atoms. We have not succeeded in preparing the corresponding silver compound.

It is noteworthy that the complex ion $[Cu(CN)_4]'''$ has exactly the same number of electrons, and presumably the same electronic distribution, as the neutral complex $[Ni(CO)_4]$ which has also been shown to be tetrahedral (Brockway and Cross, *loc. cit.*).

Tetrakisthioacetamide-cuprous chloride forms tetragonal crystals which Laue photographs and the absence of pyroelectric effects (by the liquid-air test) show to belong to the alternating (C'_4) class. Since the body-centred cell is found to contain two molecules, each complex ion possesses alternating tetragonal symmetry. This symmetry is consistent with either a planar or a tetrahedral distribution of the four Cu–S bonds, and the tetrahedral configuration has in this case been established by intensity measurements. Symmetry considerations fix the copper atoms at (000) and ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) in the structure, and there are two possibilities for the positions of the chlorine ions, *viz.*, (*a*) ($0\frac{1}{2}\frac{1}{4}$) and ($\frac{1}{2}0\frac{3}{4}$) or (*b*) ($00\frac{1}{2}$) and ($\frac{1}{2}\frac{1}{2}0$). The remaining atoms lie on general positions. With a planar distribution of sulphur atoms either (*a*) or (*b*) is possible for the chlorine ions, whereas on account of the relatively short length of the *c*-axis (5·52 A.) only (*a*) is possible with a tetrahedral configuration.

A preliminary survey of the intensities, assisted by interatomic distances known from previous work, enables the range of permissible structures to be restricted very considerably. Thus, it is found possible to account for the *relative* intensities of the orders of (001) by means of a structure in which the sulphur atoms are all coplanar with the copper atom, provided that the chlorine ions are situated in the positions (*b*); on the other hand, to account for the weakness of the odd orders of (110), the chlorine ions must be in the positions (*a*). The mutually contradictory nature of these results excludes the planar configuration completely; measurement of *absolute* intensities [by standardisation against the (400) rock-salt reflection], however, not only furnishes further convincing evidence against the planar arrangement, but enables the details of the tetrahedral structure to be found with reasonable precision. The following table gives a comparison of the experimental structure factors for {001} (col. 2) with the theoretical figures for the best possible planar arrangement (col. 3) and for the tetrahedral structure finally adopted (col. 4). It is clear that the planar structure is impossible.

hkl.	*F* (obs.).	*F* (planar).	*F* (tetrahedral).
002	64	126	76
004	70	134	82
006	28	70	32

The final tetrahedral structure is shown projected on (001) in the figure; Table II shows the comparison between the observed absolute *F*'s for {*hk*0} planes and those calculated from this structure. It will be seen that the general agreement is very good, the only considerable divergence being in the case of the (400) reflection. We are unable to account

TABLE II.

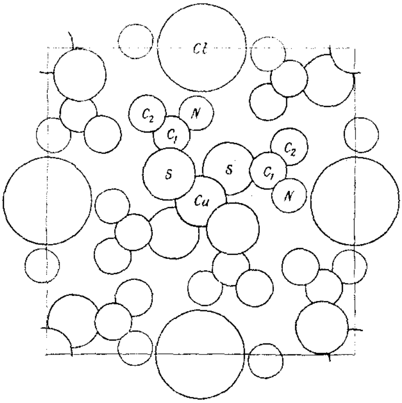
hkl.	*F* (obs.).	*F* (calc.).	*hkl.*	*F* (obs.).	*F* (calc.).	*hkl.*	*F* (obs.).	*F* (calc.).
110	54	89	550	30	38	400	<12	49
220	40	65	660	68	87	600	<14	10
330	31	39	770	31	39	800	81	68
440	81	113	200	50	67			

for this discrepancy, which, however, in view of the excellence of the remaining results, cannot be regarded as requiring more than miuor adjustments of the atomic positions.

The tendency for the observed structure factors to be low is probably to be accounted for by the formation on the crystals of a superficial layer of cuprous chloride which would increase their absorption coefficient, possibly by as much as 10%. The following table gives the co-ordinates of the atoms in one of the four thioacetamide groups attached to the copper atom at (000); the co-ordinates of the three atoms in the other three thioacetamide groups of the same complex corresponding to an atom at (xyz) in the first group are ($\bar{x}\bar{y}z$), ($y\bar{x}\bar{z}$), and ($\bar{y}x\bar{z}$). The co-ordinates of the second complex in the unit cell are derived by a translation of ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$). As previously mentioned, the co-ordinates of

S	(0·106 0·088 0·219)	C_2..................	(0·177 0·285 0·415)
C_1..................	(0·100 0·216 0·256)	N	(0·016 0·285 0·138)

the chlorine ions are ($0\frac{1}{2}\frac{1}{4}$) and ($\frac{1}{2}0\frac{3}{4}$). Each chlorine is surrounded approximately tetrahedrally by four amino-groups. The principal interatomic distances in the complex are Cu–S = 2·10 A., S–C = 1·60 A., C–C = 1·54 A., and C–N = 1·48 A. Other distances are NH_2 . . . . Cl = 3·40 A. and CH_3 . . . . CH_3 = 3·55 A.



Tetrakisthioacetamide-argentous chloride is fully isomorphous with the copper derivative, its structure differing only in the metal–sulphur distance (Ag–S = 2·20 A.). The following table shows the agreement between some observed and calculated structure factors [in this case relative, F(440) being taken as standard].

hkl.	*F* (obs.).	*F* (calc.).	*hkl.*	*F* (obs.).	*F* (calc.).	*hkl.*	*F* (obs.).	*F* (calc.).
110	130	130	550	71	56	400	24	71
220	87	105	660	81	81	600	45	33
330	35	67	200	96	100	800	112	90
440	160	160						

A detailed Fourier analysis of these two substances will be published later.

Experimental.

Potassium Cuprocyanide.—Freshly precipitated cuprous cyanide was dissolved in a slight excess of concentrated aqueous potassium cyanide, and the solution evaporated in a desiccator over phosphoric oxide. Large colourless crystals of the double cyanide separated [Found: Cu, 22·38; CN, 35·0. Calc. for $K_3Cu(CN)_4$: Cu, 22·31; CN, 36·5%].

Tetrakisthioacetamide-cuprous Chloride (II).—This was prepared according to the method of

Kurnakow (*Ber.*, 1894, **27**, 46), by boiling together aqueous solutions of cupric chloride (1·5 g.; 10 c.c.) and thioacetamide (3 g.; 10 c.c.). After removal of the black precipitate initially formed, the solution was set aside, and colourless crystals of the required compound separated [Found: Cu, 15·91; N, 14·18. Calc. for $CuCl(C_2H_5NS)_4$: Cu, 15·93; N, 14·03%]. This compound dissolves readily in alcohol, but is insoluble in other organic solvents; the aqueous solution decomposes on heating, with separation of copper sulphide.

Tetrakisthioacetamide-argentous Chloride (as II).—To an aqueous solution of silver nitrate (1·5 g.; 10 c.c.) was added a slight excess of aqueous thioacetamide (3 g.; 10 c.c.), followed by about 10 c.c. of 10% ammonium chloride; the mixture was heated nearly to boiling, and filtered. Colourless needles of the *silver* derivative separated on standing [Found: Ag, 24·22; Cl, 8·12. $AgCl(C_2H_5NS)_4$ requires Ag, 24·31; Cl, 8·00%].

Picolinic acid and potassium picolinate were prepared by oxidation of α-picoline by means of potassium permanganate as described by Weidel (*Ber.*, 1879, **12**, 1992).

Argentic Picolinate.—This compound was prepared by Barbieri's method (*Atti R. Accad. Lincei*, 1933, **17**, 1078): an aqueous solution of silver nitrate (1·7 g.; 50 c.c.) was added to picolinic acid (3·7 g.) in 50 c.c. of water, the precipitate redissolved by sodium carbonate (2·5 g.), and treated with a solution of ammonium persulphate (1·7 g.; 60 c.c.), orange-red needles of the argentic compound separating [Found: Ag, 30·54; N, 8·1. Calc. for $Ag(C_6H_4O_2N)_2$: Ag, 30·66; N, 7·9%].

α-Cupric Picolinate.—An aqueous solution of potassium picolinate (7·0 g.; 20 c.c.) was added to a hot aqueous copper acetate solution (4 g.; 50 c.c.), and on cooling deep-blue crystals of cupric picolinate dihydrate were obtained [Found: Cu, 18·55. Calc. for $Cu(C_6H_4O_2N)_2,2H_2O$: Cu, 18·50%]. When dried at 110° for a few hours it lost its water of crystallisation and left the anhydrous substance as a lavender-blue powder [Found: Cu, 20·62; N, 9·1. Calc. for $Cu(C_6H_4O_2N)_2$: Cu, 20·66; N, 9·1%]. The anhydrous compound melts at 298° (decomp.); it is slightly soluble in alcohol, readily soluble in phenol giving a deep-blue solution, but insoluble in other organic media. When shaken with excess of warm alcoholic thiourea, a turquoise-blue *compound* is formed [Found: Cu, 14·10; N, 18·3. $Cu(C_6H_4O_2N)_2,2CS(NH_2)_2$ requires Cu, 13·83; N, 18·1%].

The molecular weight of the picolinate was determined cryoscopically in phenol (constant = 7·27° per 1000 g.) (*M*, calc., = 307·6):

c (g./1000 g.)	6·735	5·901
Δt	0·163°	0·138°
M	300·2	310·3

β-Cupric Picolinate.—Solutions of copper acetate (2 g.; 25 c.c.) and potassium picolinate (3·5 g.; 10 c.c.) in absolute alcohol were mixed and kept. From the deep-blue solution a microcrystalline precipitate rapidly separated [Found: Cu, 20·56; N, 8·9. $Cu(C_6H_4O_2N)_2$ requires Cu, 20·66; N, 9·1%], m. p. 285° (decomp.); it is slightly soluble in alcohol, and in water gives the dihydrate. The molecular weight of this form of cupric picolinate could not be determined, since in the only solvent available (*viz.*, phenol) reversion to the α-form occurred (identified by the thiourea reaction). Treated with excess thiourea in absolute alcohol, it afforded a powder-blue *compound* [Found: Cu, 16·41; N, 14·9. $Cu(C_6H_4O_2N)_2,CS(NH_2)_2$ requires Cu, 16·56; N, 14·6%].

Nickel Picolinate.—A hot concentrated aqueous solution of picolinic acid was neutralised with nickel carbonate and filtered. On cooling, *nickel picolinate tetrahydrate* separated in small blue prisms [Found: Ni, 15·56. $Ni(C_6H_4O_2N)_2,4H_2O$ requires Ni, 15·66%]. When dried at 105°, it lost $2H_2O$, leaving the dihydrate, which became anhydrous after drying for 6 hours at 140°. When alcoholic solutions were used, the product had a very variable composition, and a second modification could not be obtained.

Platinous Picolinate.—Hot aqueous solutions of picolinic acid (1·6 g.; 5 c.c.) and potassium chloroplatinite (2 g.; 15 c.c.) were mixed; after a few minutes the platinum derivative separated as pale yellow microscopic needles [Found: Pt, 44·43; N, 6·3. Calc. for $Pt(C_6H_4O_2N)_2$: Pt, 44·42; N, 6·4%]. This is almost insoluble in water and organic solvents except phenol. When warmed on the water-bath with aqueous ethylenediamine, it slowly dissolved, and the product, after acidification with hydrochloric acid, gave the violet plato-salt $[Pt\,en_2][PtCl_4]$ with potassium chloroplatinite (Found: Pt, 59·69. Calc.: Pt, 59·82%), indicating that the picolinate groups are in *trans*-positions.

Palladous Picolinate.—Addition of aqueous picolinic acid to potassium chloropalladite immediately gave a cream-coloured precipitate of the *palladium* compound [Found: Pd,

30·41; N, 7·8. $Pd(C_6H_4O_2N)_2$ requires Pd, 30·42; N, 8·0%]. This compound closely resembles the platinum compound in its solubility, and *X*-ray powder photographs show that the two are isomorphous but quite unlike either the silver or the copper derivative. It dissolved in aqueous ethylenediamine and treatment as above afforded the plato-salt $[Pd\,en_2][PtCl_4]$ as pink needles (Found: Pt + Pd, 53·56. Calc.: Pt + Pd, 53·56%).

Crystallographic and X-Ray Results.

All *X*-ray measurements were made with copper-K_α radiation upon single crystals unless otherwise stated. Refractive indices (determined by immersion methods) are for sodium light.

Potassium Cuprocyanide.—Occurs in colourless rhombohedral crystals exhibiting the form {110} and occasionally {100} very small. The crystals are strongly pyroelectric. The cell dimension is a = 8·00 A. and $\alpha = 77° 32'$. The number (n) of molecules in the unit cell is 2, whence d(calc.) = 2·06 g./c.c. (obs. 2·07).

There are no halvings, and Laue photographs show D_{3d} symmetry. The space-group is therefore $R32$ (D_3^7), and each complex ion has a three-fold axis of symmetry. The cyanide groups must therefore be arranged tetrahedrally around the copper atom, or have the very improbable distribution of three in a plane and the fourth at right angles.

Refractive indices: $\omega = 1·552 \pm 0·003$ and $\varepsilon = 1·544 \pm 0·003$. These figures differ considerably from the earlier values of Grailich (1858; see Groth, I, 317).

Tetrakisthioacetamide-cuprous Chloride.—The crystals of this substance are colourless tetragonal combinations of a{100}, m{110}, and r{101}, elongated parallel to the c-axis. The cell dimensions are a = 12·43 and c = 5·52 A.; n = 2; d(calc.) = 1·56 g./c.c. (obs. 1·56).

Abnormal spacings: {hkl} absent when $h + k + l$ is odd.

The crystals are non-pyroelectric and Laue photographs show C_{4h} symmetry. The space-group is therefore $I\bar{4}$ ($C_4'^2$) and each complex ion has a four-fold alternating axis of symmetry, which is compatible with either a planar or a tetrahedral distribution of copper valencies. Refractive indices: $\omega = 1·775 \pm 0·005$ and $\varepsilon = 1·755 \pm 0·005$.

Tetrakisthioacetamide-argentous Chloride.—This compound crystallises in thin colourless needles exhibiting the same forms as the copper derivative, with which it is isomorphous. The cell dimensions are a = 12·59 and c = 5·37 A.; n = 2; d(calc.) = 1·67 g./c.c. (obs. 1·69).

Abnormal spacings: {hkl} absent when $h + k + l$ is odd. The space-group is $I\bar{4}$ and the complex ion has a four-fold alternating axis of symmetry.

α-Cupric Picolinate.—*Dihydrate.* This substance crystallises in very thin, blue, six-sided, triclinic plates. The cell dimensions are a = 7·80, b = 10·75, c = 5·10, d_{010} = 8·87 A. and $\beta = 108° 40'$; α and γ were not determined; n = 1; d(calc.) = 1·71 g./c.c. (obs. 1·71).

The crystals are not pyroelectric; they are therefore pinakoidal, so that the molecules are centro-symmetrical, *i.e.*, the picolinate groups are in *trans*-planar positions. The possibility of an octahedral arrangement, in which the water molecules are co-ordinated to the copper atom, is excluded by the shortness of the [c] axis (5·10 A.); the ease with which this substance loses its water also renders co-ordination improbable.

Refractive indices: $\alpha < 1·50$, $\gamma > 1·76$.

Anhydrous salt. This powder retains the form of the original dihydrate crystals. Refractive indices: $\alpha \leqslant 1·54$, $\gamma \geqslant 1·76$.

β-Cupric Picolinate.—Occurs in small blue needles showing straight extinction. Refractive indices: $\alpha \leqslant 1·56$, $\gamma \geqslant 1·78$.

Argentic Picolinate.—Small needles showing inclined extinction. Powder photographs show that this compound is isomorphous with the anhydrous α-cupric picolinate and Table I gives the principal lattice spacings of the two compounds. Refractive indices: $\alpha \leqslant 1·50$, $\gamma \geqslant 1·76$.

Intensity Measurements.—Absolute integrated intensities of the reflections from the tetrakisthioacetamide-cuprous chloride were obtained by direct comparison with the (400) reflection from a rock-salt crystal the cube face of which had been specially ground as recommended by Bragg and West (*Z. Krist.*, 1928, **69**, 122), who record accurate measurements of the absolute intensity of this reflection ($\rho = 0·98 \times 10^{-4}$ for Mo-K_α). Large crystals were used, the incident *X*-ray beam being defined by narrow vertical slits. The two reflections were recorded on the same photograph, and the stronger reduced by means of absorbing screens of aluminium foil until approximately equal in intensity to the weaker. An accurate comparison of the photographic blackness of the resulting spots was then obtained photometrically. The reduction due to the known thickness of aluminium foil could be calculated accurately, and hence the intensities for the copper compound obtained with reasonable precision.

To obtain uniform exposures, the X-ray tube (a Metalix tube with half-wave rectification) was run under as steady conditions as possible, the actual exposure being determined by a prepayment meter of the ordinary type in the primary circuit of the H.T. transformer. Careful and repeated tests showed that this procedure could be relied upon to give X-ray exposures reproducible within less than 5%. No allowance for extinction has been made. The experimental structure factors (F) are then calculated from the observed absolute integrated intensities ρ by means of the formula

$$\rho = \frac{1}{2\mu}\left[\frac{Ne^2F}{mc^2}\right]^2 . \lambda^3 . \frac{1 + \cos^2 2\theta}{2 \sin 2\theta}$$

where μ is the linear absorption coefficient of the crystal for X-rays of wave-length λ, and the other constants have their usual significance. The atomic scattering factors of James and Brindley (*Z. Krist.*, 1931, **78**, 470) have been used in calculating the F values for the proposed structure.

SUMMARY.

By X-ray methods the picolinic acid derivatives of bivalent copper and silver are found to possess a planar structure, but potassium cuprocyanide and the tetrakisthioacetamide derivatives of cuprous and argentous chlorides are shown to exhibit tetrahedral configurations. The structures of the last two compounds are worked out in detail.

The importance of the principal valency of a metal atom in determining the configuration of its quadricovalent derivatives is emphasised.

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THE UNIVERSITY, EDGBASTON, BIRMINGHAM. [*Received, April 24th*, 1936.]

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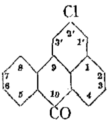
179. *The Direct Synthesis of 2′-Halogeno*meso*benzanthrones.**

By I. M. HEILBRON, R. N. HESLOP, and F. IRVING.

NUMEROUS examples are to be found, especially in the patent literature, of the formation of *meso*benzanthrone and its derivatives by condensation of αβ-unsaturated aldehydes and ketones with anthraquinone and its reduction products. With the object of extending this reaction to the synthesis of 2′-chloro*meso*benzanthrone (I) it was decided to attempt the condensation of anthrone with chloromalondialdehyde, which reacts in its enol-form as an αβ-unsaturated aldehyde and is readily available from αβγγ-tetrachloro-Δ^{α}-propylene according to Prins's method (*J. pr. Chem.*, 1914, **89**, 414). In practice it has been found unnecessary to isolate the aldehyde, since 2′-chloro*meso*benzanthrone is readily produced by the direct interaction of anthrone and the chloro-olefin in warm concentrated sulphuric acid. It is probable that the liberation of hydrogen chloride which occurs during the reaction is due entirely to the hydrolysis of the tetrachloropropylene to chloromalondialdehyde, which immediately condenses with the anthrone, although the possibility that condensation may commence with the intermediate αβ-dichloroacraldehyde cannot be completely eliminated.



(I.)

The structure of the 2′-chloro*meso*benzanthrone (m. p. 191—192°), which appears to be identical with the *Bz*-2-chlorobenzanthrone (m. p. 190°) obtained by Kalle and Co. (Sw.P. 122,904; *Chem. Zentr.*, 1928, **99**, I, 1100) by a tedious synthesis from 1′-nitro*meso*benzanthrone, has been confirmed during the present investigation by its direct synthesis from 2′-amino*meso*benzanthrone.

αβγγ-Tetrachloro-Δ^{α}-propylene reacts equally well with substituted anthrones; *e.g.*, 1 : 4- and 1 : 5-dichloroanthrone give respectively 2′ : 5 : 8- and 2′ : 4 : 8-*trichloro*meso*benzanthrone*. From 4-chloroanthrone, two isomeric dichloro*meso*benzanthrones are theoretically obtainable, and these have been isolated in approximately equal amounts,

* The compound hitherto known as "benzanthrone" will in future be named "*meso*benzanthrone."—Ed.

their separation depending upon their differing solubility in benzene. By oxidation to the corresponding chloroanthraquinone-1-carboxylic acid by the method of Perkin and Spencer (J., 1922, **121**, 478), the more soluble compound, m. p. 240°, was shown to be 2′ : 5-*dichloro*-meso*benzanthrone*, and the less soluble isomeride, m. p. 203—204°, the 2′ : 4-*dichloro*-derivative.

The chlorine atom in 2′-chloro*meso*benzanthrone is extremely unreactive and all attempts to replace it by a methoxy-, cyano-, or amino-group have given unsatisfactory results. On the other hand, alcoholic potash fusion under the normal conditions employed for the preparation of dibenzanthrones readily yields a purple vat dye, which, however, is almost devoid of chlorine. The behaviour of the di- and tri-chloro*meso*benzanthrones mentioned above on fusion with alcoholic potash has led to the interesting observation that, whereas both the 2′ : 5-dichloro- and the 2′ : 5 : 8-trichloro-compound readily undergo conversion into dibenzanthrones, the isomeric 2′ : 4-dichloro- and 2′ : 4 : 8-trichloro-*meso*benzanthrones fail to do so. From this it would appear that the introduction of the *op*-directive group into the 4-position in the *meso*benzanthrone molecule inhibits the reactivity of the hydrogen atom in position 2 sufficiently to prevent fusion to the di-molecule.

An attempt has also been made to apply the new *meso*benzanthrone synthesis described above to the preparation of 2′-bromo*meso*benzanthrone. By analogy this would involve the preparation of αβγγ-tetrabromo-Δ^{α}-propylene from the corresponding *s.*-pentabromopropane. According to Prins (*loc. cit.*) the latter is formed by the condensation of *s.*-dibromoethylene with bromoform in presence of anhydrous aluminium bromide. The comparative inaccessibility of the last two reagents led us to explore alternative routes and the following was adopted: dibromoethylene was condensed with chloroform in the presence of anhydrous aluminium chloride and the product, presumably αγγ-trichloro-αβ-dibromopropane, was converted by alcoholic potash into a substance which, judged from analytical data, was a mixture of the three theoretically possible compounds CHCl:CBr·CHBrCl, CHBr:CBr·$CHCl_2$, and CHCl:CBr·$CHCl_2$. When this was hydrolysed with concentrated sulphuric acid, bromomalondialdehyde was obtained in high yield, the presence of a bromine atom in the β-position in all the propylene derivatives present thus being established.

Condensation of the mixture of halogenated propylenes with anthrone under the conditions described in the case of αβγγ-tetrachloro-Δ^{α}-propylene proved abortive owing to the liberation of bromine and extensive oxidation of the anthrone to anthraquinone. Eventually a method was evolved whereby the propylene was first hydrolysed to bromomalondialdehyde, which, without isolation, was condensed with anthrone in the sulphuric acid solution in presence of sulphur dioxide, giving a bromo*meso*benzanthrone (A), m. p. 174—175°, at first thought to be the anticipated 2′-bromo-derivative. Its general properties, however, *e.g.*, its deep red-violet solution in concentrated sulphuric acid, in contrast with the orange-red colour of all the 2′-chloro*meso*benzanthrones, and its extremely facile conversion into a cyano*meso*benzanthrone having the same melting point as that recorded in G.P. 476,118 for 1′-cyano*meso*benzanthrone, led us to consider the possibility of its being actually 1′-bromo*meso*benzanthrone. That this view was correct was shown by the preparation of 1′-bromo*meso*benzanthrone by direct bromination of *meso*benzanthrone (compare G.P. 193,959), the product having the same m. p. whether heated alone or mixed with (A). The identity of (A) as 1′-bromo*meso*benzanthrone was further confirmed by the direct synthesis of both 2′-*bromo*meso*benzanthrone*, m. p. 194—195°, and 2′-*cyano*meso*benzanthrone*, m. p. 285—286°, from 2′-amino*meso*benzanthrone.

The unexpected formation of 1′-bromo*meso*benzanthrone may be due to migration of the bromine atom or to the complete elimination of bromine at an intermediate stage of the condensation with the formation of *meso*benzanthrone itself, which is then attacked by the displaced bromine in the normal 1′-position.

EXPERIMENTAL.

s.-*Pentachloropropane*.—Prins (*loc. cit.*) gives no details of the preparation. The following procedure was found satisfactory: A mixture of dry chloroform (150 g.) and *s.*-dichloroethylene

(60 g.) was slowly added with cooling and stirring to an intimate suspension of powdered aluminium chloride (15 g.) and fine white sand (60 g.) in chloroform (20 g.). After 20 hours' stirring at 30°, the product was decomposed with water, and the chloroform layer separated. After removal of solvent from the washed and dried solution, the residual oil was fractionated under reduced pressure, *s*.-pentachloropropane being collected as a heavy colourless liquid, b. p. 98—100°/20 mm. (yield, 63% calc. on the dichloroethylene).

αβγγ-Tetrachloro-Δ^{α}-propylene was conveniently prepared by treatment of *s*.-pentachloropropane with the requisite amount of alcoholic potassium hydroxide. After several hours the solution was filtered, the alcohol removed, and the residual oil fractionally distilled, the tetrachloropropylene being obtained as a colourless heavy oil, b. p. 165—167° (yield, 70%).

*Preparation of the 2′-Chloro*meso*benzanthrones.*—The following general procedure was employed: A solution of the anthrone (1 part) in concentrated sulphuric acid (8 parts) was treated with a slight excess of αβγγ-tetrachloro-Δ^{α}-propylene, added during 15 minutes, the temperature being maintained first at 40° for 16 hours and then at 50° for 6 hours, with continuous stirring. A vigorous evolution of hydrogen chloride occurred and the solution gradually became orange or red. The cold product was poured on ice and the crude *meso*benzanthrone was collected, washed with water, and extracted with boiling dilute sodium hydroxide solution (2%) to remove unchanged anthrone and sulphonation products.

*2′-Chloro*meso*benzanthrone.* (1) The dark green reaction product obtained as described above was washed by decantation with boiling alcohol, whereby easily soluble impurities were removed, and then exhaustively extracted with benzene, the insoluble black residue being rejected. The crude 2′-chloro*meso*benzanthrone (yield, 30%) obtained on concentration of the benzene solution was repeatedly crystallised from the same solvent, from which it separated in yellowish-green plates, m. p. 191—192°. Its solution in concentrated sulphuric acid was deep orange-red with a brown fluorescence (Found: C, 77·0; H, 3·6; Cl, 13·7. Calc. for $C_{17}H_9OCl$: C, 77·1; H, 3·4; Cl, 13·4%). Potash fusion at 220° for 15 minutes yielded a dibenzanthrone almost free of chlorine, dyeing cotton a deep purple shade from a red-violet vat (Found: Cl, 2·7. Calc. for $C_{34}H_{14}O_2Cl_2$: Cl, 13·5%).

(2) 2′-Amino*meso*benzanthrone (24·5 g.), prepared from 2′-nitro*meso*benzanthrone by reduction with sodium sulphide, was dissolved in concentrated sulphuric acid (250 g.), and sodium nitrite (10·5 g.) added during 2 hours with stirring, the temperature being maintained at 5—10°. After a further 2 hours, the solution was diluted with ice-water (250 c.c.) and kept over-night in an ice-chest. The partly separated diazonium sulphate was completely precipitated by further dilution with ice-water (200 c.c.), collected, and made into a fine paste with concentrated hydrochloric acid (100 c.c.). This was added with rapid stirring at 30—35° during 1 hour to a solution of freshly prepared cuprous chloride (20 g.) in hydrochloric acid (600 c.c. of 17%) and after a further 3 hours the temperature was raised to 70—80°. The crude product was collected and extracted successively with hot dilute nitric acid to remove copper salts, with boiling aqueous sodium hydroxide to remove traces of 2′-hydroxy*meso*benzanthrone, and with water. It was crystallised first from benzene and finally from glacial acetic acid, from which it separated in yellowish-green needles, m. p. 192—193°, giving no depression on admixture with the benzanthrone described above.

*2′ : 5 : 8-Trichloro*meso*benzanthrone.* The required 1 : 4-dichloroanthrone was prepared as described by Barnett and Wiltshire (*Ber.*, 1929, **62**, 1971). The crude reaction product, after removal of soluble impurities with hot alcohol, was repeatedly crystallised from benzene, pure 2′ : 5 : 8-*trichloro*meso*benzanthrone* being obtained in golden-yellow needles, m. p. 180—181° (yield, 75%) (Found: C, 61·0; H, 2·2; Cl, 31·7. $C_{17}H_7OCl_3$ requires C, 61·2; H, 2·1; Cl, 31·9%). On fusion with alcoholic potash it yields a dibenzanthrone which dyes cotton a red-violet shade from a clear blue vat.

*2′ : 4 : 8-Trichloro*meso*benzanthrone,* prepared from 1 : 5-dichloroanthrone (Barnett and Matthews, J., 1923, **123**, 2553), separated from benzene or xylene in yellow nodules, m. p. 190—191° (yield, 60%) (Found: C, 61·1; H, 2·4; Cl, 31·2%). Its solution in concentrated sulphuric acid was deep red with a brown fluorescence.

*2′ : 4- and 2′ : 5-Dichloro*meso*benzanthrones.* The required 4-chloroanthrone was prepared according to Barnett and Matthews's method (*loc. cit.*). The dark green reaction product (yield, 85%) was exhaustively extracted with boiling benzene, leaving a black residue (5%) which was not further examined. The combined extracts were concentrated; 2′ : 4-*dichloro*meso*benzanthrone* then separated and after recrystallisation from the same solvent was obtained in yellow-green needles, m. p. 203—204°. It dissolved in concentrated sulphuric acid to an intense orange-red solution with a yellow fluorescence (Found: C, 68·1; H, 2·5; Cl, 24·1. $C_{17}H_8OCl_2$

requires C, 68·2; H, 2·7; Cl, 23·7%). On oxidation with chromic acid in glacial acetic acid solution (Perkin and Spencer, *loc. cit.*) it yielded a chloroanthraquinonecarboxylic acid (pale yellow crystals, m. p. 231—232°), the methyl ester of which (yellow needles, m. p. 185—186°) showed no depression in m. p. when mixed with authentic methyl 4-chloroanthraquinone-1-carboxylate kindly supplied by Professor Simonsen.

Further concentration of the benzene mother-liquor from which the above benzanthrone had separated gave 2' : 5-*dichloro*meso*benzanthrone* in hard green nodules, m. p. 240°. Its solution in concentrated sulphuric acid was indistinguishable from that of the 2' : 4-isomeride (Found : C, 68·3; H, 2·8%). Chromic acid oxidation gave a chloroanthraquinonecarboxylic acid, separating from glacial acetic acid in yellow needles, m. p. 312—313°. The methyl ester (pale yellow needles, m. p. 183°) showed no depression when melted with authentic methyl 5-chloroanthraquinone-1-carboxylate (compare Cahn, Jones, and Simonsen, J., 1933, 444).

Bromomalondialdehyde from s.-*Dibromoethylene.*—*s.*-Dibromoethylene was condensed with chloroform in presence of aluminium chloride as described in the preparation of *s.*-pentachloropropane. The $\alpha\gamma\gamma$-trichloro-$\alpha\beta$-dibromopropane, obtained as a heavy colourless liquid, b. p. 130—133°/30 mm. (yield, 70% calc. on the dibromoethylene), was treated with alcoholic potassium hydroxide, giving the mixed chlorobromopropylenes, b. p. 195—202°. These (15 g.) were stirred for 16 hours at 30—40° with concentrated sulphuric acid (50 c.c.) and the mixture was diluted with water (200 c.c.) and cooled to 5°. The separated bromomaldondialdehyde was recrystallised from benzene, giving long needles (4·7 g.), m. p. 139—140°. Dieckmann and Platz (*Ber.*, 1904, 37, 4638) give m. p. 140° (Found: C, 23·9; H, 2·0; Br, 52·9. Calc. for $C_3H_3O_2Br$: C, 24·1; H, 2·1; Br, 53·0%).

Owing to its appreciable solubility in water, only a partial isolation of the aldehyde is effected by the above method. The following modification was adopted for its complete isolation: The acid reaction mixture was diluted with ice-water (100 c.c.) and treated with a solution of aniline hydrochloride (9 g.) in water (200 c.c.); α-bromo-β-anilinoacraldehyde (10·5 g.) separated on standing. It crystallised from alcohol in long colourless needles, m. p. 162°, giving no depression on admixture with the compound, m. p. 164°, described by Beattie, Heilbron, and Irving (J., 1932, 260).

Condensation of the Chlorobromopropylenes with Anthrone.—The chlorobromopropylenes (6 g.) were hydrolysed as described above with concentrated sulphuric acid (36 g.), sulphur dioxide was then rapidly passed through the red-brown solution for 15 minutes, the temperature being simultaneously raised to 60°, and a solution of anthrone (5 g.) in concentrated sulphuric acid (20 g.) was added in four equal portions during 2 hours. After being maintained at 60° for a further 10 hours, the red solution was poured on ice and the precipitated dark green solid was collected and washed, first with hot dilute sodium hydroxide solution to remove sulphonation impurities, and then with water. The dried product was exhaustively extracted with boiling glacial acetic acid; when the combined extracts were concentrated, crude 1'-bromo*meso*benzanthrone separated. The pure compound crystallised from glacial acetic acid in golden-yellow plates, m. p. 174—175° (G.P. 193,959 gives the m. p. as 170°) (Found: C, 66·1; H, 3·1; Br, 25·7. Calc. for $C_{17}H_9OBr$: C, 66·0; H, 2·9; Br, 25·9%).

1'-*Cyano*meso*benzanthrone.*—The above bromobenzanthrone (2 g.) was refluxed in phenylacetonitrile solution (30 c.c.) with freshly prepared cuprous cyanide (1 g.) for 12 hours. After cooling, the separated solid was collected, washed with alcohol, repeatedly boiled with dilute nitric acid to remove copper salts, and dried. On recrystallisation, first from glacial acetic acid and finally from nitrobenzene, 1'-cyano*meso*benzanthrone was obtained in pale yellow needles, m. p. 242—243°, which dissolved in concentrated sulphuric acid to an intense orange solution with a characteristic yellow-green fluorescence.

2'-*Bromo*meso*benzanthrone*, prepared by the addition of *meso*benzanthrone-2'-diazonium sulphate to a solution of cuprous bromide in 15% hydrobromic acid solution according to the method given for 2'-chloro*meso*benzanthrone, separated from glacial acetic acid in bright yellow needles, m. p. 194—195°. Its solution in concentrated sulphuric acid was orange-red, like that of 2'-chloro*meso*benzanthrone (Found: C, 66·0; H, 3·0; Br, 26·1. $C_{17}H_9OBr$ requires C, 66·0; H, 2·9; Br, 25·9%). On alcoholic potash fusion a dibenzanthrone was produced, which dyed cotton a bluish-purple shade from a red-violet vat.

2'-*Cyano*meso*benzanthrone.*—A suspension of *meso*benzanthrone-2'-diazonium sulphate (prepared from 2'-amino*meso*benzanthrone, 24·5 g.) in water (150 c.c.) was added during one hour with rapid stirring to a solution of potassium cyanide (62·5 g.) and copper sulphate (57·5 g.) in water (400 c.c.), the temperature being maintained at 30—35°. After a further 3 hours, the temperature was slowly raised to 80° and the crude reaction product was collected and washed

first with boiling dilute nitric acid and then with water. After repeated crystallisation from nitrobenzene, 2′-*cyano*meso*benzanthrone* was obtained in pale yellow needles, m. p. 285—286°; its solution in concentrated sulphuric acid was orange-yellow with an intense yellow fluorescence (Found: C, 84·2; H, 3·4. $C_{18}H_9ON$ requires C, 84·6; H, 3·5%).

meso*Benzanthrone*-2′-*carboxylic Acid*.—A solution of 2′-cyano*meso*benzanthrone (3 g.) in glacial acetic acid (60 c.c.) was refluxed for 16 hours with 50% sulphuric acid (48 c.c.). The reaction mixture, after cooling to 60°, was treated with sodium nitrite (1·5 g.) during one hour with rapid stirring, to decompose any amide. The carboxylic acid, precipitated with water and dried, crystallised from nitrobenzene in pale lemon-yellow needles, m. p. 341—342° (Schaarschmidt, *Ber.*, 1917, **50**, 294, gives m. p. 347°) (Found: C, 78·8; H, 3·8. Calc. for $C_{18}H_{10}O_3$: C, 78·8; H, 3·6%). The *ethyl* ester prepared by passing dry hydrogen chloride into a boiling suspension of the acid in absolute alcohol for 12 hours, separated from the same solvent in long yellow needles, m. p. 172—173° (Found: C, 79·2; H, 4·7. $C_{20}H_{14}O_3$ requires C, 79·4; H, 4·6%).

The authors are indebted to Imperial Chemical Industries, Ltd., for a grant.

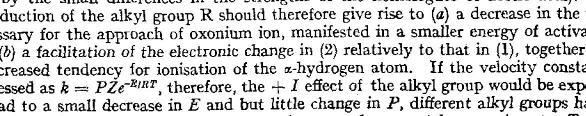
THE UNIVERSITY, MANCHESTER. [*Received, April 2nd*, 1936.]

180. *The Influence of Alkyl Groups upon Reaction Velocities in Solution. Part I. The Acid-catalysed Prototropy of Phenyl Alkyl Ketones.*

By DAVID P. EVANS.

THE acid-catalysed prototropy of a series of nuclear-substituted acetophenones, $CH_3{\cdot}CO{\cdot}C_6H_4X$, has recently been discussed by Evans, Morgan, and Watson (J., 1935, 1167) in the light of the mechanism put forward by Watson, Nathan, and Laurie (*J. Chem. Physics*, 1933, **3**, 170). On their view, a fruitful collision between ketone and catalyst leads to the formation of a bond at the carbonyl oxygen with resultant electronic activation expressed as $>C{=}O \longrightarrow >\overset{+}{C}{-}\overset{-}{O}$. This energised form may then revert to the original ketone, or may be transformed into enol. The velocity of prototropic change therefore depends upon (*a*) the rate of reaction between ketone and catalyst and (*b*) the proportion of semipolar form which changes into enol.

The present communication deals with the acid-catalysed prototropy (measured by Lapworth's bromination method) of a series of phenyl *n*-alkyl ketones, $CH_2R{\cdot}CO{\cdot}C_6H_5$, extending from acetophenone to *n*-hexophenone, and also of *iso*butyrophenone. On Watson, Nathau, and Laurie's scheme, the mechanism of the change is represented by



the later stages (1) and (2) being alternative (compare Evans, Morgan, and Watson, *loc. cit.*, p. 1170).

Alkyl groups are weakly electron-repulsive, and to much the same extent (as shown, *e.g.*, by the small differences in the strengths of the homologues of acetic acid). The introduction of the alkyl group R should therefore give rise to (*a*) a decrease in the work necessary for the approach of oxonium ion, manifested in a smaller energy of activation, and (*b*) a facilitation of the electronic change in (2) relatively to that in (1), together with a decreased tendency for ionisation of the α-hydrogen atom. If the velocity constant is expressed as $k = PZe^{-E/RT}$, therefore, the $+I$ effect of the alkyl group would be expected to lead to a small decrease in E and but little change in P, different alkyl groups having similar effects. These predictions are not, however, borne out by experiment. Table I records the values of the velocity coefficients (expressed as fall in $N/50$-thiosulphate titre

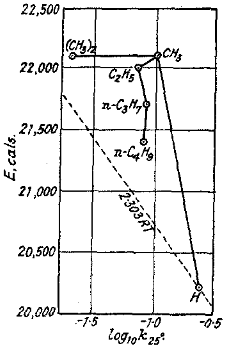
per minute for 20 c.c. of 0·1*M*-ketone solutions in 75% acetic acid containing 0·5*M*-hydrochloric acid), the energies of activation calculated in the usual manner, and the values of *P* calculated on the assumption that $[H^{\cdot}] = [HCl]$.

TABLE I.

Bromination of Phenyl Alkyl Ketones, $CH_2R\cdot COPh$.

R.	$k_{25°}$.	$k_{35°}$.	$k_{45°}$.	*E* (cals.).	*P*.
H	0·241	0·739	2·14	20,200	0·15
CH_3	0·104	0·352	1·12	22,100	1·53
C_2H_5	0·0721	0·244	0·774	22,000	0·85
n-C_3H_7	0·0851	0·284	0·875	21,700	0·59
n-C_4H_9	0·0817	0·267	0·824	21,400	0·32
($CH_2R = CHMe_2$)	0·0213	0·0728	0·231	22,100	0·30

There is a marked fall in velocity with increasing length of the straight alkyl chain up to *n*-butyrophenone; α-methyl, indeed, has a greater effect than *p*-nitro (Evans, Morgan, and Watson, *loc. cit.*). As the alkyl series is ascended, however, the velocity coefficients tend to a limiting constant value, but *iso*butyrophenone reacts more slowly than any of the other ketones; these results resemble those of Bennett and Reynolds (J., 1935, 131) for the reaction of hydrogen bromide with aliphatic alcohols. In passing from acetophenone (R = H) to propiophenone ($R = CH_3$) there is a marked increase in energy of activation, accompanied by a considerable rise in *P* (roughly 10-fold). Further lengthening of the straight alkyl chain causes a small, yet continuous decrease in *E* with simultaneous decrease in *P*. These changes are illustrated diagrammatically in the figure; the graphical method of Hinshelwood and his collaborators (J., 1935, 587, 1111, 1147, 1588), here employed, is based on the equation $E = c - 2\cdot303RT \cdot \log k$, which holds when *P* is constant.

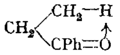


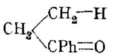
Changes in Energy of Activation.—The large increase in *E* in passing from acetophenone to propiophenone is unexpected both in magnitude and in direction, and it indicates the operation, in the latter compound, of a factor (or factors) of considerable magnitude in addition to the inductive effect. An apparent explanation of this increased energy of activation for propiophenone (and the higher phenyl *n*-alkyl ketones) is obtained from the recent postulates of Baker and Nathan (J., 1935, 1844) regarding the capacity for electron-release by alkyl groups attached to conjugate systems, —C→C=O. On their view, the introduction of an alkyl group at the α-carbon of acetophenone would cause a decrease in this electron-release with a resultant rise of *E*. The approximate constancy of the (higher) energy of activation for propio-, *n*-butyro- and *n*-valero-phenones (one α-hydrogen atom replaced) is in harmony with this view. On the other hand, the observation that the energies of activation for propiophenone and *iso*butyrophenone (two α-hydrogen atoms replaced) are almost identical is not expected on Baker and Nathan's postulates, which, moreover, do not provide an interpretation of the considerable increase in the *P* factor in passing from aceto- to propio-phenone.

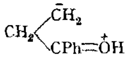
The similarity in the values of *E* for propio-, *n*- and *iso*-butyro-phenones shows that the larger activation energy (greater than that for acetophenone by approximately 2000 cals.) results from the introduction of the first methyl at the α-carbon atom. It is suggested, therefore, that in these (and higher) ketones a β-hydrogen atom co-ordinates with the unshared electrons of carbonyl oxygen, giving (I), with a resultant increase in

the work necessary for the approach of oxonium ion to form the activated complex.* Such interaction between a methyl group and the unshared electrons of a nitrogen atom is indicated by the smaller co-ordinating power of α-picoline and dimethyl-*o*-toluidine than of pyridine and dimethylaniline respectively (Klaus and Baudisch, *Ber.*, 1918, **51**, 1036; 1921, **54**, 413; who speak of a "neutralisation" between tertiary nitrogen and methyl), and by the different dipole moments of quinoline and 2 : 6-dimethylquinoline (Le Fèvre and Le Fèvre, J., 1935, 1471). Earp and Glasstone (J., 1935, 1709) have recently formulated the compounds of chloroform with acetone and quinoline in a similar way.

The above suggestion postulates the two-covalency of hydrogen, which is now regarded as a resonance phenomenon (Sidgwick, *Ann. Reports*, 1934, **31**, 43); in the present case the "unperturbed forms" would be (II) and (III). By using the interatomic distances


(I.)


(II.)


(III.)

C—C (aliphatic) 1·53, and C=O 1·25 A. (Robertson, *Chem. Reviews*, 1935, **16**, 434) and assuming the valency angle between the carbonyl bond and an alkyl chain to be 125° and that between the valencies of the chain as 109°, calculation gives the following approximate values for the minimum distances (*d*) between the centres of the oxygen and the terminal carbon atoms of the alkyl chain in the phenyl *n*-alkyl ketones :

Alkyl group, R	(H)	CH_3	C_2H_5	C_3H_7	C_4H_9
d, A.	2·5	2·8	2·1	0·7	1·1

The distances of the α- and the β-carbon atoms from the oxygen are very similar to those between the two oxygens linked through co-ordinate hydrogen in sodium bicarbonate (2·55 A., Zachariasen, *J. Chem. Physics*, 1933, **1**, 634), and between the two fluorine atoms in the anion of the "acid" fluorides (2·36 A., *idem, ibid.*). This fact favours the possibility of resonance in the ketones. The absence of such resonance in acetophenone, indicated by the lower energy of activation, is probably due to the instability of a four-membered chelate ring; for this reason also it must be supposed that the β- and not the α-hydrogen atom in propiophenone (and the other ketones) is concerned. The "activation" of the hydrogen necessary to make resonance possible may be ascribed to the inductive effect (— *I*) of carbonyl (cf. the high dipole moments of ketones), which will probably be transmitted to the β-carbon atom to a sufficient extent. Steric considerations also show that this atom is likely to be concerned in all the ketones, for only here is there a linear disposition of the carbon, hydrogen, and oxygen atoms (which is necessary for the two-covalency of hydrogen, Sidgwick, *Ann. Reports*, 1933, **30**, 113). Further, the radii 0·75 A. and 0·5 A. being assumed for carbon and oxygen respectively, there is insufficient space between γ-carbon and carbonyl oxygen for an intervening hydrogen atom of radius 0·6 A. If this resonance phenomenon involves the β-carbon atom in every case, the approximate constancy of the activation energy for propiophenone and the higher ketones receives a simple explanation.†

The view here presented is also in harmony with the results of Hinshelwood and Legard (J., 1935, 587, 1588) for the acid-catalysed esterification of trimethylbenzoic and trimethylacetic acids, where the methyl groups again lead to a large increase in *E*. The dissociation constant of the latter acid, however ($K \times 10^5 = 0{\cdot}978$, Billitzer, *Monatsh.*, 1899, **20**, 670; cf. $K \times 10^5 = 1{\cdot}8$ for acetic acid), is interpretable solely on the basis of

* A "direct" effect opposite in sign to the inductive effect has been ascribed to methyl by Lapworth and Manske (J., 1928, 2539) and by Bennett and Mosses (*J.*, *1930*, *2366*; compare Kenner and Morton, J., 1934, 679).

† There is actually a very small but continuous *decrease* in *E* for the ketones above propiophenone. This may be due to the slowly increasing inductive effect of the alkyl group, as found from studies of unsymmetrical mercury and lead alkyls (Kharasch and Flenner, *J. Amer. Chem. Soc.*, 1932, **54**, 686; Jones, Evans, Gulwell, and Griffiths, J., 1935, 43).

the inductive effect of methyl. The operation of the factor discussed above is no doubt prevented here by the resonance of the carboxyl group, which removes ketonic properties. The addition of an acid catalyst will, however, eliminate the resonance normally associated with carboxyl, and hence acid-catalysed esterification is comparable with the prototropy of ketones. Lowry (*J.*, 1925, **127**, 1381) has, indeed, suggested that the organic acid shows a " development of its ketonic functions " in catalysed esterification reactions.

Changes in the Probability Factor.—A ten-fold increase of the P factor in passing from acetophenone to propiophenone appears sufficiently large to warrant theoretical deductions. It has already been pointed out that the introduction of α-methyl will result in a definite increase in the proportion of the energised form which changes to enol (see p. 785). Further, the inductive effect of the alkyl group R will be reinforced by the distortion of the electronic system of carbonyl oxygen due to the co-ordination of β-hydrogen. The total electron-repulsion may therefore be of sufficient magnitude to account for the large change in P (compare the important effects of methyl groups upon the velocity and the mechanism of hydrolysis of alkyl halides; Hughes and Ingold, J., 1935, 244). Higher *n*-alkyl groups will have a similar effect.

The relatively small but continuous decrease in P when the chain is further lengthened may be ascribed to steric hindrance of the true geometric type, which causes (*inter alia*) a decrease in the probability of obtaining the correct orientation of the ketone molecule at the moment of impact with oxonium ion.

Further studies are being carried out on the bromination of alkyl substituted acetophenones.

EXPERIMENTAL.

(All temperatures are corrected.)

Preparation of Materials.—*Phenyl alkyl ketones.* Acetophenone was distilled twice under reduced pressure and was further purified by freezing. The specimen used had m. p. 19·6°, $n_D^{20°}$ 1·5328, $d_{4°}^{20°}$ 1·0289. *n*-Propiophenone was twice recrystallised from light petroleum, and the last traces of solvent were removed by vacuum distillation; m. p. 18·6°, $n_D^{20°}$ 1·5269, $d_{4°}^{20°}$ 1·0105 (Wagner, *J. Russ. Phys. Chem. Soc.*, 1884, **16**, 325, gives m. p. 18·5°). *n*-Butyrophenone was prepared by the Friedel–Crafts reaction from *n*-butyryl chloride and purified by several distillations in a vacuum; m. p. 12·2°, $n_D^{20°}$ 1·5196 (Elson, Gibson, and Johnson, J., 1930, 1129, give m. p. 13°); *semicarbazone, m. p.* 191·5° (Stadnikow, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 462, gives m. p. 188—189°); 2 : 4-*dinitrophenylhydrazone*, orange-red plates from aqueous acetic acid, m. p. 190° (Found : C, 58·7; H, 5·0. $C_{16}H_{16}O_4N_4$ requires C, 58·5; H, 4·9%). *iso*Butyrophenone, prepared in similar manner from *iso*butyryl chloride, had b. p. 97·5°/10 mm., $n_D^{20°}$ 1·5190; semicarbazone, m. p. 181·5° (Lapworth and Steele, J., 1911, **99**, 1885, give m. p. 181°); 2 : 4-*dinitrophenylhydrazone*, orange-yellow plates from aqueous acetic acid, m. p. 163° (Found : C, 58·2; H, 4·6%).

n-Valerophenone was obtained in good yield by refluxing benzonitrile with a slight excess of *n*-butylmagnesium bromide in ether, decomposing the mixture with dilute sulphuric acid, and steam-distilling the product; b. p. 130°/16 mm., $n_D^{20°}$ 1·5150; semicarbazone, needles from aqueous alcohol, m. p. 166° (Layroud, *Bull. Soc. chim.*, 1906, **35**, 224, gives m. p. 166°); 2 : 4-*dinitrophenylhydrazone*, bright red needles from glacial acetic acid, m. p. 166° (Found : C, 59·5; H, 5·4. $C_{17}H_{18}O_4N_4$ requires C, 59·65; H, 5·3%). *n*-Hexophenone, prepared by the Friedel–Crafts method, was steam-distilled from an equal volume of 10% sodium hydroxide solution and recrystallised from alcohol, m. p. 27° (Sabatier and Mailhe, *Compt. rend.*, 1914, **158**, 834, give m. p. 27°); semicarbazone, m. p. 133° (Schroeter, *Ber.*, 1907, **40**, 1603, gives m. p. 132°); 2 : 4-*dinitrophenylhydrazone*, thick, red needles from glacial acetic acid, m. p. 168° (Found : C, 60·6; H, 5·8. $C_{18}H_{20}O_4N_4$ requires C, 60·7; H, 5·6%).

Velocity Determinations.—The reaction medium (75% acetic acid containing 0·5*M*-hydrochloric acid) was prepared at 25°, 35°, and 45° by adding the necessary volume of constant-boiling hydrochloric acid to 750 c.c. (at the temperature of the bath) of acetic acid purified by the method of Orton and Bradfield (J., 1927, 983), and diluting to 1 litre at the temperature of the bath with conductivity water. The medium did not react measurably with bromine during 2—3 days. Solutions containing 0·1*M*-ketone and about 0·005*M*-bromine were made up in the medium at each temperature in 100 c.c. (or 50 c.c.) flasks, and the reactions were followed by withdrawing 20 c.c. (10 c.c.) at intervals and adding it to 80 c.c. (40 c.c.) of aqueous

potassium iodide containing a 50% excess over the anticipated titre. The liberated iodine was titrated against *N*/50-thiosulphate. In the case of the four higher phenyl alkyl ketones, after addition of starch, the end-point was observed by adding 5 c.c. of carbon tetrachloride to the liquid, closing the mouth of the flask tightly with a rubber stopper, and shaking well after each addition of thiosulphate. The tetrachloride dissolves the bromo-ketone, which otherwise clouds the liquid in the titration flask in addition to adsorbing small quantities of iodine.

The author records his indebtedness to Dr. H. B. Watson for his invaluable criticism and encouragement, and to Imperial Chemical Industries, Ltd., for grants.

TECHNICAL COLLEGE, CARDIFF. [*Received, February 27th*, 1936.]

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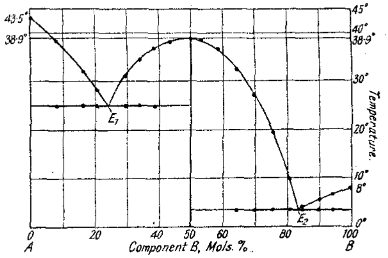
181. *Some Binary Systems of Organic Compounds. Thermal Analyses and Specific Refractivities.*

By W. R. BURNHAM and W. M. MADGIN.

As a preliminary to further studies of equilibrium constants in terms of activities (Glass and Madgin, J., 1934, 1292 and earlier), six binary systems (Figs. 1, 2, and 3), not hitherto reported, have been investigated by the methods of thermal analysis. Baud (*Bull. Soc. chim.*, 1913, **13**, 435) has reported the f. p.'s of mixtures of acetic acid with chlorobenzene

FIG. 1.

Freezing point–composition diagram.



A. p-*Toluidine* : E_1 = 24% (*mol.*) *of B* (25·2°).
B. o-*Chlorophenol* : E_2 = 83·6% (*mol.*) *of B* (3·6°).

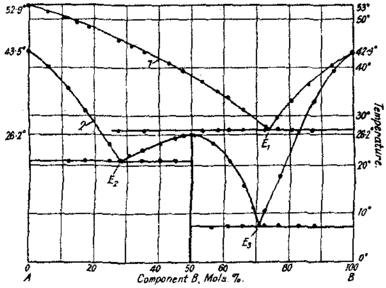
(covering a range of composition from 100% to 65% of acetic acid by weight), but his results are insufficient to show the type of the system. Pushin and Matavulj (*Z. physikal. Chem.*, 1931, **158**, 290, and subsequently) have studied the variation of refractive index with composition in binary systems as a means of typifying the systems, and similar studies have been included in the present investigations.

EXPERIMENTAL.

The starting materials were "Purified" reagents. Their further purification has been described previously (Glass and Madgin, *loc. cit.*); except that acetic acid was purified by freezing and fractional distillation (Bousfield and Lowry, J., 1911, **99**, 432), chlorobenzene was dried over phosphoric oxide and fractionally distilled, and *p*-chlorophenol was fractionally frozen (down to a f. p. 42·5°) and the solid phase was separated and fractionally distilled, b. p. 216°/740 mm.: all operations upon the last substance were carried out in a current of dried air.

Fig. 2.

Freezing point–composition diagrams.



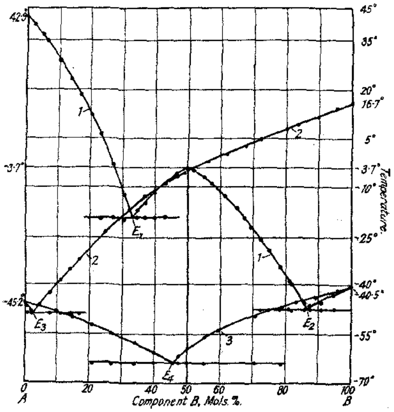
1. *A*. p-*Dichlorobenzene.* *B*. p-*Chlorophenol.*

2. p-*Toluidine.* p-*Chlorophenol.*

E_1 = 73·4%(*mol.*) *of B* (27·2°).
E_2 = 28% (*mol.*) *of B* (21°).
E_3 = 71% (*mol.*) *of B* (7·4°).

Fig. 3.

Freezing point–composition diagrams.



1. *A*. p-*Chlorophenol.* *B*. *Pyridine.*

2. *Chlorobenzene.* *Acetic Acid.*

3. *Chlorobenzene.* *Pyridine.*

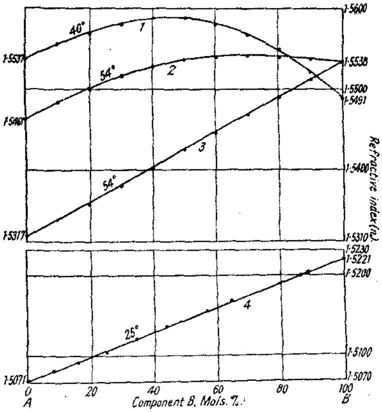
E_1 = 33·4% *of B* (− 19·5°); E_2 = 86·5% *of B* (− 47·3°); E_3 = 3% *of B* (− 48·5°); E_4 = 46% *of B* (− 63·5°).

The thermal analyses of the binary systems now reported were carried out as previously described (Glass and Madgin, J., 1934, 260), but with the system pyridine–chlorobenzene it was necessary to cool with liquid air in the determination of f. p.'s below − 65°.

Of the six systems now reported (Figs. 1, 2, and 3), three are of the simple eutectic type, *viz.*, *p*-dichlorobenzene–*p*-chlorophenol, pyridine–chlorobenzene, and acetic acid–chlorobenzene. The other three systems (*p*-toluidine–*o*-chlorophenol, *p*-toluidine–*p*-chlorophenol, and *p*-chlorophenol–pyridine) definitely indicate the formation of stable equimolecular compounds. When possible this was confirmed by isolating solid phases from numerous melts during the thermal analyses. The contaminating solutions were removed by pressing on porous plates, and the resulting solids had the f. p.'s of the corresponding compounds.

Fig. 4.

Refractive index–composition diagrams.



1.	2.	3.	4.
A. p-*Toluidine.*	p-*Toluidine.*	p-*Dichlorobenzene.*	*Pyridine.*
B. o-*Chlorophenol.*	p-*Chlorophenol.*	p-*Chlorophenol.*	*Chlorobenzene.*

Pushin and Matavulj (*Z. physikal. Chem.*, 1933, **164**, 80) state that the system *p*-chlorophenol–pyridine cannot be determined by thermal analysis, owing to the persistence of supercooling in most mixtures, but their refractive-index determinations show the existence of an equimolecular compound. When an equimolecular mixture of *p*-chlorophenol and pyridine is prepared at the ordinary temperature, considerable heat is developed and a homogeneous liquid formed. This liquid becomes excessively viscous when cooled below − 20° but it shows no tendency to solidify; however, when kept at about − 8° for several hours, it solidifies and the solid then has a definite m. p., *viz.* − 3·7°. A mobile liquid is formed on melting.

With mixtures containing 0—30% or 90—100% of pyridine the f. p.'s were readily determined, generally by inoculation with pure components, but no eutectic arrests were observed even on cooling to quite low temperatures. By using the solid equimolecular compound (cf. above) as inoculating phase, it was possible to determine eutectic arrests and to investigate the complete diagram (Fig. 3).

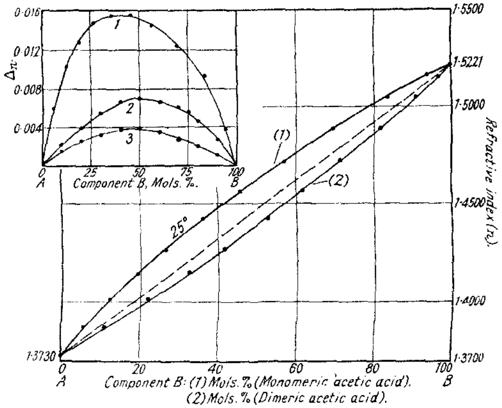
The two systems illustrated in Fig. 2 support Kendall and Booge's conclusion (*J. Amer. Chem. Soc.*, 1916, **38**, 1712) that, when a compound is formed (*p*-toluidine with *p*-chlorophenol), the f. p. of a pure component (*p*-chlorophenol) is depressed more than when a simple eutectic system is formed.

Refractive Indices.—The variation of refractive index with composition has been examined

for the different systems, over a range of temperature, by means of an Abbé refractometer. Sodium light was employed. Apart from a general decrease of refractive index with rising temperature, no notable variations with temperature were found. Representative results are shown in Figs. 4 and 5, but no significance attaches to the particular temperatures selected.

FIG. 5.

Refractive index–composition diagrams.



Inset.	1.	2.	3.
	A. Acetic Acid.	p-*Toluidine.*	p-*Toluidine.*
	B. Chlorobenzene.	o-*Chlorophenol.*	p-*Chlorophenol.*

A. = Acetic acid. *B. = Chlorobenzene.*

DISCUSSION.

The thermal analyses seem to point definitely to the conclusions already stated, but the system acetic acid–chlorobenzene merits comment. This is a eutectic system, and the form of the curve (Fig. 3) is the same as that reported by Kendall and Booge (*loc. cit.*) for the system chloroacetic acid–benzene. These authors consider such curves to indicate an ideal solution.

The refractivity results shown in Fig. 4 accord with the views of Pushin and Matavulj (*loc. cit.*), *viz.*, that in systems where compound formation occurs, the refractivity curve shows positive deviations from the mixture law (cf. curves 1 and 2), but with eutectic systems, the refractivity curves follow the mixture law or show negative deviations. Curves 3 and 4 show no deviations. The results in Fig. 4 are similar if weight or volume compositions are used instead of molecular compositions.

When refractivity is plotted against simple molecular composition (monomeric) for the system acetic acid–chlorobenzene (Fig. 5), positive deviations are observed although this is a eutectic system. The inset of Fig. 5 shows the deviations in this system compared with those in two systems involving compound formation. Baud (*loc. cit.*) considers that acetic acid exists as double (dimeric) molecules in chlorobenzene, and, by using molecular compositions of mixtures in terms of dimeric acetic acid, curve 2 of Fig. 5 is obtained. The curves for both weight and volume compositions practically coincide with this, and Pushin and Matavulj (*Z. physikal. Chem.*, 1932, **162**, 415) anticipated that curves for molecular

and for weight compositions should be similar. The mixture-law curve (broken line, Fig. 5) evidently corresponds to molecular compositions in terms of mixed monomeric and dimeric acetic acid. This probably represents the statistical average of the compositions, and the relative proportions of each form will vary continually with dilution. The possibility of higher polymerides is not excluded, and pure acetic acid is no doubt a complicated mixture of various polymerides: its vapour is widely regarded as composed largely of dimeric molecules at the ordinary temperature.

Further work on similar eutectic systems is needed.

One of us (W. R. B.) is indebted to the Council of Armstrong College for a Research Studentship.

ARMSTRONG COLLEGE (UNIVERSITY OF DURHAM),
NEWCASTLE-UPON-TYNE. [*Received, March 28th, 1936.*]

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182. *Amidines. Part I. The Synthesis of Symmetrical and Unsymmetrical Benzenyldiphenylamidines, and New Reactions of Amidines.*

By S. P. JOSHI, A. P. KHANOLKAR, and T. S. WHEELER.

Synthesis of s-*Benzyldiphenylamidines.*—Limpricht (*Annalen*, 1865, **135**, 82; cf. Doebner, *Ber.*, 1882, **15**, 233; *Annalen*, 1883, **217**, 241) found that *s*-benzenyldiphenylamidine could be obtained directly from benzotrichloride and aniline, but, although the usual methods for the production of amidines involve two or three stages from the initial amines, this reaction does not seem to have been further investigated, possibly because it tends to be vigorous unless properly controlled. It has now been found that, in presence of nitrobenzene, benzotrichloride reacts smoothly with a number of primary arylamines to give the corresponding *s*-benzyldiphenylamidines in yields which range up to 85%. s-*Benzenyldi*-p- and -m-*nitrophenyl*-, -m-*tolyl*-, -p-*chlorophenyl*-, and -*s*-*tribromophenyl-amidine* have thus been prepared, but satisfactory results could not be obtained with benzidine, *m*-nitro-*p*-toluidine, *o*-nitro-*p*-toluidine, *p*-nitro-*o*-toluidine, and 2 : 4-dinitroaniline. With *o*-nitroaniline a product of unknown constitution was obtained which is being further investigated.

The reaction probably involves the intermediate formation of a benzanilideimidochloride, for, if moisture is present, a benzanilide is formed, and further, a small yield of the unsymmetrical amidine, *benzenyl*-N-p-*chlorophenyl*-N'-*phenylamidine*,* has been obtained from benzotrichloride, *p*-chloroaniline, and aniline.

$$Ph{\cdot}CCl_3 \xrightarrow{NH_2R} Ph{\cdot}CCl_2{\cdot}NHR \longrightarrow Ph{\cdot}CCl{:}NR \xrightarrow{NH_2R} PhC{\cdot}(NHR){:}NR$$

$$Ph{\cdot}CO{\cdot}NHR \xleftarrow{H_2O} \;\big|\; \xrightarrow{NH_2R'} Ph{\cdot}C(NHR'){:}NR$$

(R, R' = aryl)

During the work it was observed that benzotrichloride reacts with acetanilide to give *s*-ethenyldiphenylamidine and benzanilide.

Synthesis of Unsymmetrical Benzenyldiphenylamidines.—For a study of the tautomerism of unsymmetrically substituted benzenylamidines, the following have been synthesised by the method of Hill and Cox (*J. Amer. Chem. Soc.*, 1926, **48**, 3216):—(A) benzenyl-*N*-*p*-chlorophenyl-*N'*-phenylamidine (see above), (B) *benzenyl*-N-p-*bromophenyl*-N'-*phenylamidine*, (C) *benzenyl*-N-p-*chlorophenyl*-N'-p-*methoxyphenylamidine*, (D) *benzenyl*-N-p-*chlorophenyl*-N'-p-*ethoxyphenylamidine*, (E) *benzenyl*-N-p-*chlorophenyl*-N'-p-*tolylamidine*, (F) *benzenyl*-N-p-*nitrophenyl*-N'-m-*nitrophenylamidine*, (G) *benzenyl*-N-p-*nitrophenyl*-N'-p-*tolylamidine*, (H) *benzenyl*-N-p-*nitrophenyl*-N'-m-4-*xylylamidine*, (I) *benzenyl*-N'-p-*chlorophenyl*-N-p-*nitrophenylamidine*, (J) *benzenyl*-N'-p-*bromophenyl*-N-p-*nitrophenylamidine*, and (K) p-*nitrobenzenyl*-N-p-*nitrophenyl*-N'-*phenylamidine*.

* This compound is also obtained by direct chlorination of *s*-benzenyldiphenylamidine.

(A) on methylation gives *benzenyl*-N-p-*chlorophenyl*-N'-*phenyl*-N-*methylamidine* and *benzenyl*-N'-p-*chlorophenyl*-N-*phenyl*-N-*methylamidine*; (B) similarly gives *benzenyl*-N-p-*bromophenyl*-N'-*phenyl*-N-*methylamidine* and *benzenyl*-N'-p-*bromophenyl*-N-*phenyl*-N-*methylamidine*. The four methyl-amidines were characterised by their synthesis from the corresponding methylaniline and benzanilideimidochloride.

Oxidation of Amidines.—*s*-Benzenyldiphenylamidine on treatment with acid potassium permanganate gives a well-crystallised product, the analytical results for which show it to be s-*diphenyldi(phenyliminobenzyl)hydrazine*:

$$2\text{Ph}\cdot\text{C}(\text{:NPh})\cdot\text{NHPh} \xrightarrow{\text{O}} \text{Ph}\cdot\text{C}(\text{:NPh})\cdot\text{NPh}\cdot\text{NPh}\cdot\text{C}(\text{:NPh})\text{Ph}$$

s-Benzenyldi-*p*- and -*m*-nitrophenylamidine give similar *products*.

Condensation of Amidines with Ethyl Chloroformate.—*s*-Benzenyldi-*m*-nitrophenylamidine condenses smoothly with ethyl chloroformate in benzene solution in presence of sodium hydrogen carbonate to give N-*carbethoxy*-s-*benzenyldi*-m-*nitrophenylamidine*, the structure of which is confirmed by the fact that it is also obtained by the action of alcohol on the unstable product formed by condensing carbonyl chloride with the amidine:

$$\text{Ph}\cdot\text{C}(\text{:NR})\cdot\text{NHR} \xrightarrow{\text{Cl}\cdot\text{CO}_2\text{Et}} \text{Ph}\cdot\text{C}(\text{:NR})\cdot\text{NR}\cdot\text{CO}_2\text{Et}$$

$$\text{Ph}\cdot\text{C}(\text{:NR})\cdot\text{NHR} \xrightarrow{\text{COCl}_2} \text{Ph}\cdot\text{C}(\text{:NR})\cdot\text{NR}\cdot\text{COCl} \xrightarrow{\text{EtOH}} \text{Ph}\cdot\text{C}(\text{:NR})\cdot\text{NR}\cdot\text{CO}_2\text{Et}$$

Similar *carbethoxy*-compounds were obtained from *s*-benzenyldi-*p*-nitrophenyl, -*m*-tolyl-, and -*p*-chlorophenyl-amidines.

EXPERIMENTAL.

* Indicates micro-analysis by Dr. Schoeller. † Indicates crystallisation from alcohol.

Synthesis of s-*Benzenyldiphenylamidines.*—s-*Benzenyldi*-p-*nitrophenylamidine*. Benzotrichloride (19 g.), *p*-nitroaniline (41 g.), and nitrobenzene (60 c.c.) were heated (calcium chloride guard) at 165° until evolution of hydrogen chloride had ceased. After 12 hours the precipitated hydrochloride was washed with acetone, the residue (34 g.) dissolved in pyridine, and the *base* precipitated by water; it separated from acetone in yellow crystals, m. p. 190° (Found: N, 15·2. $C_{19}H_{14}O_4N_4$ requires N, 15·5%). The amidine was also obtained by heating benzo-*p*-nitroanilideimidochloride [from benzo-*p*-nitroanilide (12 g.) and phosphorus pentachloride (11 g.)], *p*-nitroaniline (4·2 g.), and diethylaniline (11·5 g.) at 100° for 3 hours; the product was poured into hydrochloric acid (20%), and the precipitated hydrochloride (7 g.) treated with pyridine. The *hydrochloride* (action of hydrogen chloride on the amidine in benzene) sintered at 265° (Found: Cl, 8·9. $C_{19}H_{14}O_4N_4$,HCl requires Cl, 8·9%). The *acetyl* derivative † (acetic anhydride–fused sodium acetate) had m. p. 182—183° (Found: * N, 14·4. $C_{21}H_{16}O_5N_4$ requires N, 13·9%). The N-*methyl* derivative was obtained by heating the amidine (5 g.) in a sealed tube for 6 hours at 120° with methyl iodide (5 c.c.). The product was extracted with acetone, and the resulting solution treated with ammonia to give the base (3·8 g.), which was crystallised from benzene–light petroleum; m. p. 188° (Found: * N, 14·9. $C_{20}H_{16}O_4N_4$ requires N, 14·9%).

s-*Benzenyldi*-m-*nitrophenylamidine* † (prepared as described for the *p*-derivative) formed yellow needles, m. p. 147—148° (Found: N, 15·2%). The *hydrochloride* (from the concentrated acid and the amidine in acetone) sintered at 275° (Found: Cl, 9·2%). The *sulphate* (from the concentrated acid and the amidine in ether) had m. p. 196° (Found: S, 6·9. $C_{19}H_{14}O_4N_4$,H_2SO_4 requires S, 6·9 %), the *acetyl* derivative † (acetic anhydride) m. p. 135—136° (Found: * N, 14·1 %), the *benzoyl* derivative † (benzoyl chloride–pyridine) m. p. 195—196° (Found: * N, 12·2. $C_{26}H_{18}O_5N_4$ requires N, 12·0%), and the *methyl* derivative † (see *p*-compound) m. p. 114—115° (Found: * N, 15·1%).

s-*Benzenyldi*-m-*tolylamidine* † was prepared (yield, 9 g.) from *m*-toluidine (32 g.), benzotrichloride (19 g.), and nitrobenzene (60 c.c.); m. p. 135° (Found: * N, 9·4. $C_{21}H_{20}N_2$ requires N, 9·3%). The N-*methyl* derivative † had m. p. 90° (Found: * N, 9·2. $C_{22}H_{22}N_2$ requires N, 8·9%).

s-*Benzenyldi*-p-*chlorophenylamidine*,† from *p*-chloroaniline (40 g.), benzotrichloride (30 g.), and nitrobenzene (25 c.c.), had m. p. 143° (Found: * N, 8·0; Cl, 20·8. $C_{19}H_{14}N_2Cl_2$ requires N, 8·2; Cl, 20·8%); yield, 78%. The amidine was also prepared (1) by Hill and Cox's method (*loc. cit.*) from benzo-*p*-chloroanilide (11·5 g.), phosphorus pentachloride (10 g.), and *p*-chloro-

aniline (6·1 g.); yield, 55%; (2) from *p*-chloroaniline (1 mol.), diethylaniline (2·5 mols.), and benzo-*p*-chloroanilideimidochloride (1 mol.; the imidochloride was prepared from benzo-*p*-chloroanilide and excess of thionyl chloride; b. p. 180—185°/5 mm.). The *amidine hydrochloride* charred above 250° (Found: Cl, 27·9. $C_{19}H_{14}N_2Cl_2$,HCl requires Cl, 28·2%). The *sulphate* had m. p. 201° (Found: Cl, 15·9. $C_{19}H_{14}N_2Cl_2,H_2SO_4$ requires Cl, 16·2%), the *benzoyl* derivative † m. p. 155—156° (Found: Cl, 15·8. $C_{26}H_{18}ON_2Cl_2$ requires Cl, 16·0%), and the *methyl* derivative † m. p. 153—154° (Found: Cl, 19·8. $C_{20}H_{16}N_2Cl_2$ requires Cl, 20·0%).

s-*Benzenyldi*-s-*tribromophenylamidine* was prepared (yield of hydrochloride, 22 g.) from *s*-tribromoaniline (34 g.), benzotrichloride (10 g.), and nitrobenzene (25 c.c.), and crystallised from acetone and acetic acid; m. p. 196—197° (Found: Br, 64·2. $C_{19}H_{10}N_2Br_6$ requires Br, 64·3%). The *acetyl* derivative (acetic anhydride–pyridine), m. p. 173—174°, was crystallised from acetone (Found: Br, 61·2. $C_{21}H_{12}ON_2Br_6$ requires Br, 60·9%), the *benzoyl* derivative (benzoyl chloride–pyridine), m. p. 235—237°, from acetic acid (Found: Br, 56·8. $C_{26}H_{14}ON_2Br_6$ requires Br, 56·5%), and the *methyl* derivative, m. p. 160—161°, from acetone (Found: Br, 62·9. $C_{20}H_{12}N_2Br_6$ requires Br, 63·2%).

Benzenyl-N-p-*chlorophenyl*-N'-*phenylamidine* † was obtained (yield, 0·5 g.) from benzotrichloride (3·9 g.), aniline (1·8 g.), *p*-chloroaniline (2·5 g.), and nitrobenzene (5 c.c.); m. p. 120—122°. Its constitution was confirmed (mixed m. p.) by comparison with the analysed product obtained by the Hill and Cox method (*loc. cit.*) from benzo-*p*-chloroanilide (2·5 g.), phosphorus pentachloride (2·5 g.), and aniline (1 g.) (Found: Cl, 11·4. $C_{19}H_{15}N_2Cl$ requires Cl, 11·6%). The amidine was also obtained by this method from benzanilide and *p*-chloroaniline, and by the imidochloride method from benzo-*p*-chloroanilideimidochloride (see above), aniline, and diethylaniline.

Chlorination of s-*Benzenyldiphenylamidine*.—A chloroform solution of *s*-benzenyldiphenylamidine (5·4 g.) obtained (78% yield) from aniline (27 g.), benzotrichloride (19 g.), and nitrobenzene (60 c.c.) was treated with chlorine (1·4 g.) at 0°. After 12 hours, the solvent was evaporated, and the residual hydrochloride was washed with acetone and treated with ammonia to separate the free base.† A mixed m. p. determination showed it to be the monochloroamidine.

Benzenyl-N-p-*chlorophenyl*-N'-*phenylamidine hydrochloride* † had m. p. 260—262° (Found: * Cl, 20·7. $C_{19}H_{15}N_2Cl$,HCl requires Cl, 20·7%), and the *benzoyl* derivative † (benzoyl chloride–pyridine) m. p. 155—156° (Found: * N, 6·4. $C_{26}H_{19}ON_2Cl$ requires N, 6·8%).

Action of Benzotrichloride on Acetanilide.—The product obtained on heating benzotrichloride (90 g.) and acetanilide (135 g.) for 3 hours at 150° was dissolved in hot alcohol, and the solution diluted with water; benzanilide (35 g.; mixed m. p.) then separated. The aqueous-alcoholic filtrate was treated with dilute sodium hydroxide solution to precipitate *s*-ethenyldiphenylamidine (42 g.; mixed m. p.).

Synthesis of Unsymmetrical Benzenyldiphenylamidines.—The Hill and Cox method (*loc. cit.*) was used throughout. Phosphorus pentachloride (1·1 mols.) and a benzanilide derivative (1 mol.) were heated together in dry benzene; when reaction was complete the required arylamine (1—1·5 mols.) was added in the cold, and the mixture boiled under reflux for 4 hours. The amidine hydrochloride which separated (60—70% yield) was converted by means of ammonia into the free base. The hydrochloride was obtained by addition of concentrated hydrochloric acid to an acetone or alcohol solution of the base; the picrate separated from mixed alcoholic solutions of the components.

Benzenyl-N-p-*bromophenyl*-N'-*phenylamidine* † (from benzanilide and *p*-bromoaniline) had m. p. 123° (Found: Br, 22·8. $C_{19}H_{15}N_2Br$ requires Br, 22·8%). The *hydrochloride* sintered at 265—266° (Found: Cl + Br, 29·5. $C_{19}H_{15}N_2Br$,HCl requires Cl + Br, 29·8%).

Benzenyl-N-p-*chlorophenyl*-N'-p-*methoxyphenylamidine* † (from benzo-*p*-anisidide and *p*-chloroaniline) had m. p. 117—119° (Found: * C, 71·2; H, 5·1; * N, 8·0; Cl, 10·3. $C_{20}H_{17}ON_2Cl$ requires C, 71·3; H, 5·1; N, 8·3; Cl, 10·6%), the *hydrochloride* m. p. 260 (Found: * Cl, 19·2. $C_{20}H_{17}ON_2Cl$,HCl requires Cl, 19·0%), and the *picrate* † m. p. 165—166° (Found: * N, 12·1. $C_{20}H_{17}ON_2Cl,C_6H_3O_7N_3$ requires N, 12·4%).

Benzenyl-N-p-*chlorophenyl*-N'-p-*ethoxyphenylamidine* † (from benzo-*p*-phenetidide and *p*-chloroaniline) had m. p. 95—98° (Found: Cl, 10·4. $C_{21}H_{19}ON_2Cl$ requires Cl, 10·1%), the *hydrochloride* m. p. 242—244° (Found: Cl, 18·7. $C_{21}H_{19}ON_2Cl$,HCl requires Cl, 18·3%), and the *picrate* † m. p. 147—148° (Found: * N, 11·9. $C_{21}H_{19}ON_2Cl,C_6H_3O_7N_3$ requires N, 12·1%).

Benzenyl-N-p-*chlorophenyl*-N'-p-*tolylamidine* † (from benzo-*p*-toluidide and *p*-chloroaniline) had m. p. 134° (Found: Cl, 10·9. $C_{20}H_{17}N_2Cl$ requires Cl, 11·1%), the *hydrochloride* † m. p.

283° (decomp.) (Found: * Cl, 20·0. $C_{20}H_{17}N_2Cl,HCl$ requires Cl, 19·9%), and the *picrate* † m. p. 189—190° (Found: * N, 12·6. $C_{20}H_{17}N_2Cl,C_6H_3O_7N_3$ requires N, 12·7%).

Benzenyl-N-p-*nitrophenyl*-N'-m-*nitrophenylamidine* † (from benzo-*m*-nitroanilide and *p*-nitroaniline) had m. p. 170° (Found: * N, 15·1. $C_{19}H_{14}O_4N_4$ requires N, 15·5%); the *hydrochloride* sintered at 238° (Found: Cl, 9·0. $C_{19}H_{14}O_4N_4,HCl$ requires Cl, 8·9%).

Benzenyl-N-p-*nitrophenyl*-N'-p-*tolylamidine* † (from benzo-*p*-toluidide and *p*-nitroaniline) had m. p. 159—160° (Found: * N, 12·8. $C_{20}H_{17}O_2N_3$ requires N, 12·7%); the *hydrochloride* † sintered at 258° (Found: Cl, 9·6. $C_{20}H_{17}O_2N_3,HCl$ requires Cl, 9·7%).

Benzenyl-N-p-*nitrophenyl*-N'-m-4-*xylylamidine* † (from benzo-*m*-4-xylidide and *p*-nitroaniline) had m. p. 143—144° (Found: * N, 12·1. $C_{21}H_{19}O_2N_3$ requires N, 12·2%); the *hydrochloride* sintered at 237° (Found: Cl, 9·6. $C_{21}H_{19}O_2N_3,HCl$ requires Cl, 9·3%).

Benzenyl-N'-p-*chlorophenyl*-N-p-*nitrophenylamidine* † (from benzo-*p*-chloroanilide and *p*-nitroaniline) had m. p. 174—175° (Found: * N, 11·8. $C_{19}H_{14}O_2N_3Cl$ requires N, 11·9%); the *hydrochloride* sintered at 272° (Found: Cl, 18·4. $C_{19}H_{14}O_2N_3Cl,HCl$ requires Cl, 18·3%).

Benzenyl-N'-p-*bromophenyl*-N-p-*nitrophenylamidine* † (from benzo-*p*-nitroanilide and *p*-bromoaniline) had m. p. 170—171° (Found: Br, 20·6. $C_{19}H_{14}O_2N_3Br$ requires Br, 20·2%); the *hydrochloride* sintered at 270° (Found: Cl + Br, 27·1. $C_{19}H_{14}O_2N_3Br,HCl$ requires Cl + Br, 26·7%).

p-*Nitrobenzenyl*-N-p-*nitrophenyl*-N'-*phenylamidine* (from *p*-nitrobenzanilide and *p*-nitroaniline) was crystallised from acetone–alcohol; m. p. 223° (Found: * N, 15·5. $C_{19}H_{14}O_4N_4$ requires N, 15·5%). The *hydrochloride* sintered at 250° (Found: Cl, 8·6. $C_{19}H_{14}O_4N_4,HCl$ requires Cl, 8·9%).

Methylation of Benzenyl-N-p-*chlorophenyl*-N'-*phenylamidine*.—The product obtained by heating the amidine (15 g.) and methyl iodide (15 c.c.) in a sealed tube for 6 hours at 105° was extracted with boiling acetone (200 c.c.), and the residue was dissolved in pyridine; *benzenyl*-N-p-*chlorophenyl*-N'-*phenyl*-N-*methylamidine*,† needles, m. p. 112°, was precipitated by addition of water to the pyridine solution. The constitution of the base was established by its synthesis from *p*-chloromethylaniline and benzanilideimidochloride in presence of diethylaniline; the m. p. of the separated methylation product was unchanged by addition of the synthetic product (Found: * C, 74·8; H, 5·4;* N, 8·4; Cl, 11·0. $C_{20}H_{17}N_2Cl$ requires C, 74·9; H, 5·3; N, 8·7; Cl, 11·1%). The *hydrochloride* † had m. p. 226° (Found: * Cl, 19·4. $C_{20}H_{17}N_2Cl,HCl$ requires Cl, 19·9%), and the *picrate* † m. p. 157—158° (Found: N,* 12·3; Cl, 6·6. $C_{20}H_{17}N_2Cl,C_6H_3O_7N_3$ requires N, 12·7; Cl, 6·5%).

Ammonia precipitated *benzenyl*-N'-p-*chlorophenyl*-N-*phenyl*-N-*methylamidine* from the acetone filtrate as an oil which solidified; after repeated crystallisation from alcohol to free it from its isomeride, it formed hexagonal plates, m. p. 102°, depressed to 83—95° on admixture with the isomeride of m. p. 112°. Its constitution was established by its synthesis (mixed m. p. comparison) from methylaniline and benzo-*p*-chloroanilideimidochloride in presence of diethylaniline (Found: * C, 74·8; 5·3; * N, 8·3%). The *picrate* † had m. p. 150—151° (Found: * N, 12·3%).

Methylation of Benzenyl-N-p-*bromophenyl*-N'-*phenylamidine*.—The procedure was the same as for the chloro-amidine. The hydriodide insoluble in acetone yielded *benzenyl*-N-p-*bromophenyl*-N'-*phenyl*-N-*methylamidine* † (constitution established by synthesis from *p*-bromomethylaniline and benzanilideimidochloride); needles, m. p. 123—124° (Found: * C, 65·9; H, 4·8; Br, 21·6. $C_{20}H_{17}N_2Br$ requires C, 65·8; H, 4·7; Br, 21·9%). The *picrate* † had m. p. 179—180° (Found: * N, 11·3. $C_{20}H_{17}N_2Br,C_6H_3O_7N_3$ requires N, 11·8%).

The acetone filtrate on basification gave *benzenyl*-N'-p-*bromophenyl*-N-*phenyl*-N-*methylamidine*, which after repeated crystallisation from alcohol formed sugar-like crystals, m. p. 120—121°, depressed to 98—112° by admixture with its isomeride. Its constitntion was established by its synthesis from methylaniline and benzo-*p*-bromoanilideimidochloride (Found: * C, 65·5; H, 4·7; Br, 21·6%). The *picrate* † had m. p. 158—159° (Found: * N, 11·4%).

Oxidation of Amidines.—s-*Diphenyldi(phenyliminobenzyl)hydrazine*. Aqueous potassium permanganate (1%; 450 c.c.) was added in small portions at 100° to *s*-benzenyldiphenylamidine (2·7 g.) dissolved in sulphuric acid (70%; 175 c.c.). The resulting solution was diluted with water, and basified with aqueous ammonia to precipitate a mixture of the oxidation product and manganese hydroxide, from which the hydrazine *derivative* (1 g.) was extracted with acetone; m. p. 112° (Found: * C, 84·0; H, 5·0; * N, 10·6. $C_{38}H_{30}N_4$ requires C, 84·2; H, 5·5; N, 10·3%).

s-*Di*-p-*nitrophenyldi*-(p-*nitrophenyliminobenzyl*)*hydrazine* was similarly prepared. Most of the oxidation product separated on dilution of the reaction mixture with water, and was re-

crystallised from alcohol–acetone; m. p. 236° (Found: * C, 63·1; H, 3·4; N, 15·6. $C_{38}H_{26}O_8N_8$ requires C, 63·2; H, 3·6; N, 15·5%).

s-*Di*-m-*nitrophenyldi*-(m-*nitrophenyliminobenzyl*)*hydrazine*, crystallised from alcohol–acetone, had m. p. 262—264° (Found: * C, 63·5; H, 3·4%).

Condensation of Amidines with Ethyl Chloroformate.—N-*Carbethoxy*-s-*benzenyldi*-m-*nitrophenylamidine*.† (1) A solution (prepared at 0°) of ethyl chloroformate (2·2 g.) and benzenyldi-*m*-nitrophenylamidine (7·2 g.) in benzene with sodium hydrogen carbonate (2·4 g.) in suspension was kept for 12 hours at room temperature and filtered. The crude *product* (4·2 g.) which remained on evaporation of the filtrate had, after recrystallisation, m. p. 153° (Found: N, 13·1. $C_{22}H_{18}O_6N_4$ requires N, 12·9%).

(2) A solution (prepared at 0°) of carbonyl chloride (0·5 g.) and *s*-benzenyldi-*m*-nitrophenylamidine (2 g.) in toluene was kept for 12 hours and filtered from the separated amidine hydrochloride. The pasty residue obtained on evaporation of the filtrate gave on recrystallisation from alcohol the same carbethoxy-derivative (mixed m. p.) as was obtained by method (1).

N-*Carbethoxy*-s-*benzenyldi*-p-*nitrophenylamidine* † (method 1) had m. p. 169—170° (Found: * N, 12·8%), N-*carbethoxy*-s-*benzenyldi*-m-*tolylamidine* † (method 1) m. p. 94—95° (Found: * N, 7·8. $C_{24}H_{24}O_2N_2$ requires N, 7·5%), and N-*carbethoxy*-s-*benzenyldi*-p-*chlorophenylamidine* † (method 1) m. p. 118—119° (Found: Cl, 17·0. $C_{22}H_{18}O_2N_2Cl_2$ requires Cl, 17·2%).

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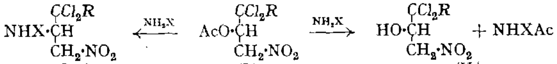
183. *The Action of Amines upon Esters. Part I.*

By HARRY IRVING.

CHATTAWAY has shown (this vol., p. 355) that the action of ammonia, *p*-toluidine, or an arylhydrazine upon certain acetic esters (I; R = Cl or CH_3·CHCl) does not proceed normally with the formation of acetamide, aceto-*p*-toluidide, or a β-acetylarylhydrazine and the liberation of the parent alcohol (II). On the contrary, the ammonia or substituted amine appears to displace the acetoxy-group with the formation of a primary amine, *N*-alkyl-*p*-toluidine, or β-alkylarylhydrazine (*III*). Thus:



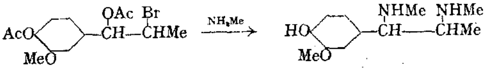
(III.) (I.) (II.)

(R = Cl, or CH_3·CHCl; X = H, *p*-CH_3·C_6H_4, or C_6H_5·NH.)

The unexpected course of these reactions is attributed to the presence of the electron-restraining (CCl_2R and NO_2) groups which, it is suggested, render the β-carbon atom in the alkyl group of the ester so kationoid that donor molecules (*i.e.*, ammonia, aniline, or hydrazine) attack the ester to a greater extent at this point than at the ketonic carbon atom of the acyl group.

Should this explanation be correct, any ester of any alcohol in which the carbon atom of the carbinol group is made sufficiently kationoid should show abnormal reactions of this novel and interesting type. In the present paper these implications have been examined and an attempt has been made to realise further examples.

A survey of the literature does not reveal many cases of reactions which belong indubitably to the abnormal type under consideration. Solomon and Sharp (J., 1931,

(IV.)  (V.)

1468), however, record that the action of dry alcoholic methylamine above 100° upon the acetoxy-bromide (IV) unexpectedly yielded the diamine (V), both the β-bromine atom and

the α-acetoxy-group having been replaced by methylamino-groups although the *p*-acetoxy-group was deacetylated in the normal manner.

The authors correlated this type of behaviour with the presence of a *p*-acetoxy-group in the aryl residue, but did not discuss in any further detail the mechanism of the amination.

The formation of methyl β-aminocrotonate and butyramide by the action of dry ammonia upon the *O*-butyrate of methyl β-hydroxycrotonate, $Me\cdot C(O\cdot CHO\cdot C_3H_7)\dot{.}C\cdot CO_2Me$, was studied by Bouveault and Bongert (*Bull. Soc. chim.*, 1902, **27**, 1051), who remarked "La formation d'une amide au moyen d'un éther dans les conditions où nous avons opéré, constitue un phénomène assez rarement observé." The formation of butyramide showed that the probable course of the reaction was simply normal amide formation, followed by the further and well-established action of ammonia upon the methyl acetoacetate thereby liberated. Methyl β-butyroxycrotonate and phenylhydrazine gave similarly β-butyrylphenylhydrazine and phenylmethylpyrazolone.

Chattaway's results are not, however, amenable to explanation in such a simple manner, for it has now been found that γγγ-trichloro-α-nitro-β-hydroxypropane (II; R = Cl), from which the reactive acetate (I; R = Cl) is derived, will not react either with phenylhydrazine or with ammonia.

On the other hand, the β-chloro-derivative, $CCl_3\cdot CHCl\cdot CH_2\cdot NO_2$, obtained by the action of phosphorous pentachloride upon this alcohol is extremely reactive. When it is treated with dry ammonia, *p*-toluidine, or phenylhydrazine in dry ethereal or alcoholic solution, much heat is evolved and the products are identical with those obtained from the same amines and the acetoxy-compound (I; R = Cl) itself.

Now since this reactive chlorine atom is attached to a carbon atom bearing electron-restraining (CCl_3,$CH_2\cdot NO_2$) groups, its ease of anionisation will be reduced. Its observed reactivity is therefore analogous to the well-established kationoid activity of picryl chloride, Pic·Cl (Pic = 2 : 4 : 6-trinitrophenyl), which with ammonia, anilines, and hydrazines yields picramide, *N*-picrylanilines, and β-picrylhydrazines respectively (cf. "Organische Chemie," Beilstein, 4th ed., vol. V, p. 274). The analogous behaviour of the two chloro-compounds suggested that picryl acetate, AcO·Pic, in which the 1-carbon atom is undoubtedly kationoid, should undergo amination reactions similar to those shown by Chattaway's acetate (I). This expectation has not, however, been realised, for the action of dry ammonia upon a solution of picryl acetate in dry ether or in dry alcohol gave only ammonium acetate and ammonium picrate, no trace of picramide being formed. Further the action of phenylhydrazine gave no β-picrylphenylhydrazine.

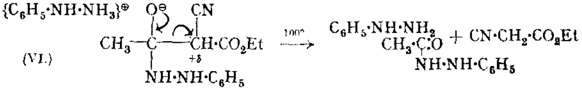
These results are difficult to reconcile with Chattaway's hypothesis, especially when it is recalled that the glycollic ester $Pic\cdot O\cdot CH_2\cdot CO_2Et$ readily yields 2 : 4 : 6-trinitrophenylhydrazine, $Pic\cdot NH\cdot NH_2$, on treatment with hydrazine (Buchner, *Ber.*, 1894, **27**, 3250), and that trinitroanisole, Pic·OMe, reacts with an alcoholic solution of phenylhydrazine to give β-picrylphenylhydrazine, $Pic\cdot NH\cdot NH\cdot C_6H_5$, even below 35° (Giua and Cherchi, *Gazzetta*, 1919, **49**, II, 156).

Since the anomalous reactions of the acetate (I) did not appear to be paralleled by those of phenolic esters, a series of aliphatic analogues of the general type AcO·CHRR′ were examined in order to determine (a) the number and (b) the type of electron-restraining groups which would suffice to induce abnormal amination reactions.

The CCl_3 group alone does not appear to confer a sufficiently kationoid character upon an attached carbon atom, for the esters βββ-trichloro-α-acetoxypropionamide, $CCl_3\cdot CH(OAc)\cdot CO\cdot NH_2$ (Pinner and Fuchs, *Ber.*, 1877, **10**, 1061), γγγ-trichloro-α-acetamido-β-acetoxypropane, $CCl_3\cdot CH(OAc)\cdot CH_2\cdot NHAc$ (Chattaway and Witherington, J., 1935, 1623), γγγ-trichloro-β-acetoxypropane, $CCl_3\cdot CH(OAc)\cdot CH_3$ (isopral), and βββ-trichloro-α-acetoxy-α-phenylethane, $CCl_3\cdot CH(OAc)\cdot C_6H_5$ (Jozitsch, *Centr.*, 1897, I, 1014), do not appear to react readily with phenylhydrazine or ammonia. βββ-Trichloro-α-acetoxy-α-methoxyethane (*O*-acetylchloral methyl alcoholate), $CCl_3\cdot CH(OAc)\cdot O\cdot CH_3$, and chloral diacetate, $CCl_3\cdot CH(OAc)_2$, are similarly inert under conditions which would suffice to initiate a reaction in the case of the acetate (I). Under more drastic conditions, phenylhydrazine yields a black coked mass: the vigorous exothermic reaction resembles closely the action of phenylhydrazine upon chloral itself and the isolation of small amounts of

β-acetylphenylhydrazine from the reaction products suggests that the detachment of the acetyl groups is a primary stage.

Esters of the type $CCl_3\cdot CH(OAc)X$ were next considered, in which the second electron-restraining group X was introduced to reinforce the effect of the CCl_3 group. Here X could be $CH_2\cdot NO_2$, as in the ester (I) originally investigated, or CN, CO_2H, CO_2R, or $>C:O$. Of these possibilities, compounds of the type $CCl_3\cdot CH(OAc)\cdot CO\cdot C_6H_5$ were not examined, since the introduction of a keto-group would undoubtedly mask the effect sought for by providing an alternative and more powerfully directing centre to which donor molecules would be attracted. This contention is supported by the action of phenylhydrazine upon ethyl acetoacetate, whereby the β-phenylhydrazone, and not the phenylhydrazide, of acetoacetic ester is formed (Nef, *Annalen*, 1891, **266**, 71; compare Knorr, *ibid.*, 1887, **238**, 146). Furthermore, the action of phenylhydrazine upon ethyl α-cyanoacetoacetate also yields no hydrazide and, despite the presence of an undoubtedly strongly kationoid α-carbon atom, the phenylhydrazine does not attack at this point either. In the cold, however, an addition compound, probably to be formulated as (VI), results. At 100° this decomposes smoothly to give ethyl cyanoacetate and β-acetylphenylhydrazine (Haller, *Compt. rend.*, 1895, **120**, 1193).



(VI.)

None of the compounds $CCl_3\cdot CH(OAc)\cdot CN$, $CCl_3\cdot CH(OAc)\cdot CO_2H$, and $CCl_3\cdot CH(OAc)\cdot CO_2Et$ reacts simply with amines in a manner similar to that observed by Chattaway. Here, however, the problem is complicated by the fact that, at some stage, intramolecular elimination of hydrogen chloride takes place in every case: the unsaturated compound thereby produced may react further with the amine and then undergo a rearrangement. Chloral acetylcyanohydrin, $CCl_3\cdot CH(OAc)\cdot CN$, for example, reacts with aniline (3 mols.) in alcoholic or ethereal solution to give a mixture of aniline hydrochloride, acetanilide, and dichloroacetanilide: *p*-toluidine yields similarly a mixture of its hydrochloride, aceto-*p*-toluidide and dichloroaceto-*p*-toluidide, hydrogen cyanide being liberated in each case.

Since these reactions do not proceed quantitatively, they cannot be said definitely to prove that at least a partial replacement of the acetoxy-group by amine does not take place as Chattaway's theory would predict, although, as Lapworth pointed out with reference to the analogous reactions of amines upon chloral cyanohydrin itself (J., 1931, 1387), such a direct replacement is exceedingly improbable. Further it is difficult to see how a primary reaction product such as $CCl_3\cdot CH(CN)\cdot NH\cdot C_6H_5$ could be resolved into the products actually isolated when the reaction is carried out in the absence of water.

O-Acetyltrichlorolactic acid, $CCl_3\cdot CH(OAc)\cdot CO_2H$, like trichlorolactic acid itself, was found to yield glyoxal phenylosazone, carbon dioxide, and phenylhydrazine hydrochloride when heated with an alcoholic solution of phenylhydrazine: with ammonia, apart from ammonium chloride, no definite products could be isolated (cf. Pinner and Fuchs, *loc. cit.*). Ethyl trichlorolactate, $CCl_3\cdot CH(OH)\cdot CO_2Et$, and phenylhydrazine in alcoholic solution gave a good yield of the yellow osazone of dichloropyruvic ester (carbethoxyglyoxal phenylosazone). These reactions are being submitted to a more detailed investigation.

A final attempt to realise an example of abnormal ester behaviour led to the examination of the dimeride of acetyl cyanide, *O*-acetylmethyltartrononitrile (VII). Despite the presence of two such powerfully electron-restraining groups as the cyano-group, this ester appeared to react normally with amines, giving with an excess of aniline, dissolved in dry ether, a 75% yield of acetanilide, with dry ammonia an 87% yield of acetamide, and, as Brunner found (*Sitzungsber. Akad. Wiss. Wien*, 1894, **103**, 661), an 83% yield of β-acetyl-

phenylhydrazine with excess of phenylhydrazine in dry ether. The course of these reactions may be represented as follows:

$$\text{(VII.)}\quad CH_3\cdot C(CN)_2\cdot O\cdot CO\cdot CH_3 \xrightarrow{NH_2X} CH_3\cdot CO\cdot NHX + CH_3\cdot C(CN)_2\cdot OH \longrightarrow$$
$$HCN + CH_3\cdot CO\cdot CN \xrightarrow{NH_2X} CH_3\cdot CO\cdot NHX + HCN$$
$$(X = H,\ C_6H_5,\ \text{or}\ NH\cdot C_6H_5)$$

The primary formation of such a compound as $CH_3\cdot C(CN)_2\cdot NHX$ predicted by the application of Chattaway's theory, apart from its inherent improbability in this reaction (cf. p. 799), is here excluded on the grounds that (a) in the absence of water such a compound could not rearrange to give $CH_3\cdot CO\cdot NHX$, and (b) the maximum yield of amide (anilide or hydrazide) on this hypothesis would be 50%, *i.e.*, less than that actually observed in three different reactions.

So far, therefore, it has not been found possible to adduce one additional and unambiguous example of the abnormal behaviour of esters recorded by Chattaway. Excluding methyl β-butyroxycrotonate, picryl acetate, and the dimeride of acetyl cyanide—all of which react "normally"—the esters discussed above are all acetates of the type $CH_3\cdot CO\cdot O\cdot CHRR'$ and may be classified in two categories: (a) those which are unreactive ($R = CCl_3$; $R' = CH_3$, $CH_2\cdot NHAc$, C_6H_5, $O\cdot CH_3$, OAc, or $CO\cdot NHAc$) and (b) those in which the β-hydrogen atom is very readily detached, thereby initiating an intramolecular elimination of hydrogen chloride ($R = CCl_3$; $R' = CN$, CO_2H, or CO_2Et).

The anomalous nitro-esters ($R = CCl_3$ or $CH_3\cdot CHCl\cdot CCl_2$; $R' = CH_2\cdot NO_2$) would appear, therefore, to belong to some intermediate category in which the β-carbon atom is sufficiently kationoid to attract donor molecules, but insufficiently so to promote a facile elimination of hydrogen chloride. The validity of Chattaway's explanation is thus seen to be dependent upon an (unlikely) very special adjustment of the electron-restraint of the attached groups R and R'.

Now the "abnormal" reactions seem to occur only when R' contains a readily ionisable hydrogen atom, and it appears from preliminary work that, under the influence of proton acceptors (ammonia, aniline, or arylhydrazine), such esters (I) readily lose acetic acid to form nitro-olefins (VIII) (compare Schmidt and Rutz, *Ber.*, 1928, **61**, 2142) to which the ammonia, aniline, or arylhydrazine then adds on (compare Wieland and Sakellarios, *Ber.*, 1919, **52**, 901). Thus:

$$\text{(I)} \xrightarrow{NH_2X} NH_3X\cdot OAc + CCl_2R\cdot CH{:}CH\cdot NO_2\ \text{(VIII)} \xrightarrow{NH_2X} \text{(III)}$$

The enhanced reactivity of the tetrachloronitroparaffin $CCl_3\cdot CHCl\cdot CH_2\cdot NO_2$, and the inertness of the parent nitro-alcohol (II) now become readily explicable. In this connection the strikingly analogous action of potassium cyanide upon α-chloro-β-benzoyl-α-phenylethane, $C_6H_5\cdot CHCl\cdot CH_2\cdot CO\cdot C_6H_5$, may be recalled, for here, as Rupe and Schneide found (*Ber.*, 1895, **28**, 960; compare Lapworth, J., 1904, **85**, 1355), the ultimate product, α-cyano-β-benzoyl-α-phenylethane, $C_6H_5\cdot CH(CN)\cdot CH_2\cdot CO\cdot C_6H_5$ is obtained, not by the direct replacement of Cl by CN, but by elimination of hydrogen chloride, followed by the addition of hydrogen cyanide to the benzylideneacetophenone, $C_6H_5\cdot CH{:}CH\cdot CO\cdot C_6H_5$, so formed.

Experimental.

The Reactions of βγγγ-Tetrachloro-α-nitropropane with Phenylhydrazine, p-*Toluidine, and Ammonia.*—7·0 G. of tetrachloro-α-nitropropane (Henry, *Bull. Acad. roy. Belge*, 1897, **34**, 568) were added slowly to 6·5 g. of phenylhydrazine in 15 c.c. of dry alcohol. Much heat was evolved and γγγ-trichloro-α-nitro-β-phenylhydrazinopropane separated. After being washed with water, it crystallised from boiling alcohol in almost colourless, six-sided prisms, with domed ends (8·8 g.; theo., 9·1 g.), m. p. 120—122° (decomp.) alone or mixed with an authentic specimen (Found: Cl, 35·4. Calc. for $C_9H_{10}O_2N_3Cl_3$: Cl, 35·6%).

γγγ-Trichloro-α-nitro-β-*p*-toluidinopropane (3·0 g.), similarly prepared by the interaction of *p*-toluidine (1·2 g.) and the nitroparaffin (2·5 g.) in 10 c.c. of dry alcohol, formed pale yellow, compact crystals, from light petroleum, m. p. and mixed m. p. 60—61° (Found: Cl, 35·9. Calc. for $C_{10}H_{11}O_2N_2Cl_3$: Cl, 35·8%).

When dry ammonia gas was passed into a cooled solution of βγγγ-tetrachloro-α-nitropropane (10 g.) in 20 c.c. of anhydrous ether (or 15 c.c. of dry alcohol), much heat was evolved and from the resulting mixture of ammonium chloride and γγγ-trichloro-α-nitro-β-aminopropane hydrochloride, the free base was isolated from the latter as described by Chattaway (*loc. cit.*), and characterised as its *N*-acetyl derivative, which formed colourless prisms from alcohol, m. p. and mixed m. p. 137° (Found : Cl, 42·8. Calc. for $C_5H_7O_3N_2Cl_3$: Cl, 42·7%).

The Interaction of Aniline and O-Acetylchloralcyanohydrin in Dry Alcohol or Ether.—Aniline (3 mols., 13·0 g.) in 10 c.c. of dry alcohol was added to chloral acetylcyanohydrin (1 mol., 10·0 g.) in 20 c.c. of alcohol. The temperature rose gradually from 12° to 52° but there was no marked evolution of hydrogen cyanide. The reaction was completed by gentle boiling for 5 minutes and after distillation of half of the alcohol under reduced pressure the product was worked up by one or other of the following procedures :

(a) More alcohol was removed until a crystalline mass (19 g., m. p. 80—100°) separated, which after five recrystallisations from absolute alcohol gave dichloroacetanilide (6·5 g. ; theo., 9·5 g.) in colourless prisms, m. p. 118° alone or mixed with an authentic specimen (compare Pinner, *Ber.*, 1877, **10**, 1061 ; Cech, *Ber.*, 1876, **9**, 337). Since only catalytically small amounts of water could have been present throughout, the formation of dichloroacetanilide, $CHCl_2{\cdot}CO{\cdot}NH{\cdot}C_6H_5$, in this yield (70%) shows that the substance $CCl_3{\cdot}CH(CN){\cdot}NH{\cdot}C_6H_5$ could not have been formed intermediately.

(b) The concentrated alcoholic solution was poured into 100 c.c. of water ; an oil then separated which almost immediately solidified to a mass of colourless crystals (14·6 g., m. p. 76—85° ; theo., for dichloroacetanilide 9·5 g. and acetanilide 6·2 g. = 15·7 g.). This solid (A) was collected, and the aqueous-alcoholic filtrate evaporated to small bulk ; the pale yellow solid which then separated was collected and crystallised four times from boiling water (charcoal), acetanilide (1·2 g.), m. p. and mixed m. p. 114°, being obtained. The solid (A) was crystallised four times from alcohol and gave 7·1 g. of dichloroacetanilide, m. p. 118° ; the more soluble fraction from the alcoholic mother-liquors melted at about 80° and contained chlorine (19·5 and 23·4% in different preparations). It appears to be identical with the substauce which Pinner (*loc. cit.*) identified tentatively with monochloroacetanilide, but which appears from the work of Kötz (*J. pr. Chem.*, 1921, **103**, 231) to be a mixture of acetanilide and dichloroacetanilide.

The Action of Phenylhydrazine upon O-Acetyltrichlorolactic Acid.—*O*-Acetyltrichlorolactic acid (2·4 g.) and phenylhydrazine (5 mols., 5·4 g.) were boiled with 15 c.c. of alcohol until the evolution of carbon dioxide ceased. The cooled solution was poured into dilute hydrochloric acid and the viscous solid which then separated was extracted with ether and dried over anhydrous sodium sulphate. Glyoxalphenylosazone (1·4 g.), left on removal of the solvent, formed yellow silky leaflets, m. p. 169—170° after two recrystallisations from alcohol (Found : N, 23·2. Calc. for $C_{14}H_{14}N_4$: N, 23·5%).

The Action of Phenylhydrazine upon Ethyl Trichlorolactate.—4·4 G. of ethyl trichlorolactate and 6·5 g. (3 mols.) of phenylhydrazine were refluxed gently with 30 c.c. of alcohol for 2 hours. The soft yellow powder (5·9 g., m. p. 220°) which separated on cooling was collected and crystallised twice from boiling alcohol and then from benzene–light petroleum, from which carbethoxyglyoxalphenylosazone separated in yellow leaflets, m. p. 225—227° (decomp.) (Found : C, 66·1 ; H, 5·8 ; N, 18·0. Calc. for $C_{17}H_{18}O_2N_4$: C, 65·8 ; H, 5·8 ; N, 18·1%). The identity of this osazone with that described by Fenton (J., 1902, **81**, 431) and Will (*Ber.*, 1891, **24**, 3833) was established by warming with aqueous-alcoholic potash for 2 hours. On acidification carboxyglyoxalphenylosazone separated ; it gave bright yellow, slender prisms, m. p. 220—224° (decomp.), from boiling chloroform (Fenton, *loc. cit.*, gives m. p. 222—224°) (Found : N, 19·8. Calc. for $C_{15}H_{14}O_2N_4$: N, 19·9%).

The Action of Dry Ammonia and Aniline upon the Dimeride of Acetyl Cyanide.—Dry ammonia gas was passed into a solution of dimolecular acetyl cyanide (VII) (1·52 g.) in 10 c.c. of dry alcohol until saturated and the whole was maintained at 25° for 12 hours. The solution was then distilled rapidly until the temperature reached 150° and the residue of acetamide was collected and crystallised from benzene (1·13 g. ; theo., 1·3 g. ; m. p. 80°).

1·7 G. (slight excess) of redistilled aniline and 1·24 g. of dimolecular acetyl cyanide were refluxed gently with 25 c.c. of anhydrous ether for 2 hours. The solvent was then distilled off and acetanilide remained (1·83 g. ; theo., 2·43 g.), m. p. 114·5° (from water).

THE OLD CHEMISTRY DEPARTMENT, OXFORD. [*Received, March 30th*, 1936.]

184. *Migration Reactions in Polycyclic Systems. Part I. The Fries Rearrangement of 4-Benzoyloxydiphenyl.*

By Donald H. Hey and E. R. Buckley Jackson.

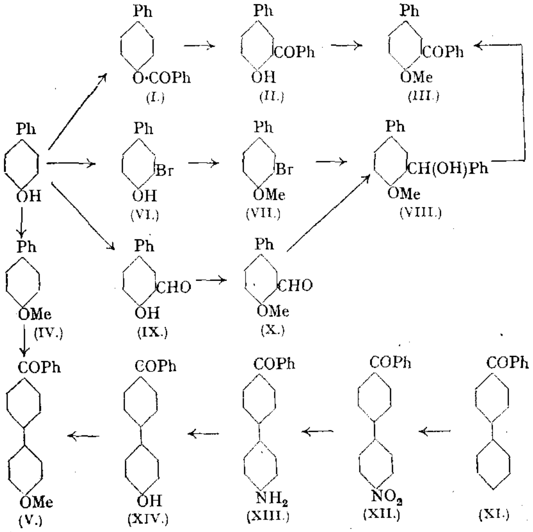
Comparatively few examples have been recorded of migration reactions, whether real or apparent, in polycyclic systems, particularly of reactions which involve a migration to one nucleus from a side chain attached to a second nucleus in the same molecule, since most migrations of this type proceed from an oxygen or a nitrogen atom attached to an aromatic nucleus which, being either potentially phenolic or basic, is particularly reactive. In the diphenyl series homonuclear migrations have been described by Bell, Kenyon, and Robinson (J., 1926, 1239) and by Scarborough and his co-workers (J., 1926, 557; 1927, 89, 3000) and the methylation of 4-aminodiphenyl hydrochloride in positions 3, 5, and 4′ by successive "migration" has been recorded by Hey and Jackson (J., 1934, 645).

Fries, von Auwers, and others have described many examples of homonuclear migration, mainly in the benzene and the naphthalene series, as the result of the action of aluminium or zinc chloride on phenolic esters whereby hydroxy-ketones are produced, but an example of heteronuclear migration of this type has been claimed by Blicke and Weinkauff (*J. Amer. Chem. Soc.*, 1932, **54**, 330) in the action of aluminium chloride on the benzoate of 4-hydroxydiphenyl. These authors draw an analogy between the Fries rearrangement of phenyl benzoate, which gives rise to *p*-hydroxybenzophenone, and that of 4-benzoyloxydiphenyl, which is stated to give rise in similar manner to 4-hydroxy-4′-benzoyldiphenyl. Proof of the identity of this compound was claimed by the fact that on methylation it gave a benzoyl-4-methoxydiphenyl identical with that obtained from the action of benzoyl chloride on 4-methoxydiphenyl in the presence of aluminium chloride. This argument, however, is unsatisfactory, since by whichever method the benzoylmethoxydiphenyl is prepared the position of attachment of the benzoyl group is uncertain. Further, many instances are on record of the production of a different aromatic hydroxy-ketone by a Fries rearrangement from that obtained by means of a Friedel–Crafts reaction on the appropriate phenol or its methyl ether (Witt and Braun, *Ber.*, 1914, **47**, 3216; Fries, *Ber.*, 1921, **54**, 709; 1925, **58**, 2835; von Auwers and Mauss, *Ber.*, 1928, **61**, 1495; *Annalen*, 1928, **464**, 293; Mosettig and Burger, *J. Amer. Chem. Soc.*, 1933, **55**, 2981). The two reactions, therefore, do not necessarily follow the same course. Other examples of the application of the Fries rearrangement to esters of polynuclear phenols have been recorded. For example, Witt and Braun (*loc. cit.*) obtained a 5% yield of 6-acetyl-2-naphthol by the action of zinc chloride on β-naphthyl acetate, although with aluminium chloride in place of zinc chloride Fries (*loc. cit.*) obtained 1-acetyl-2-naphthol. In the reactions studied by Mosettig and Burger (*J. Amer. Chem. Soc.*, 1933, **55**, 2981; 1934, **56**, 1745) in the phenanthrene series, by Wojahn (*Arch. Pharm.*, 1933, **271**, 417) in the diphenylmethane series, and by Harris and Christiansen (*J. Amer. Pharm. Assoc.*, 1934, **23**, 530) on various esters of 2- and 3-hydroxydiphenyl, only products formed by homonuclear migration were encountered. Instances of heteronuclear migration in the Fries reaction are thus very rare and it therefore seemed not improbable that the product of the rearrangement studied by Blicke and Weinkauff (*loc. cit.*) is not 4-hydroxy-4′-benzoyldiphenyl but rather 4-hydroxy-3-benzoyldiphenyl.

A reinvestigation of the Fries rearrangement of 4-benzoyloxydiphenyl (I), as carried out by Blicke and Weinkauff, was therefore undertaken. Instead of the one product (m. p. 193—195°) claimed by these authors, we obtained two, namely, 4-hydroxydiphenyl (m. p. 165°) and *4-hydroxy-3-benzoyldiphenyl* (II) (m. p. 89°), the latter yielding *4-methoxy-3-benzoyldiphenyl* (III) (m. p. 93°) on methylation. The presence of 4-hydroxydiphenyl in the product is not unexpected, since the free phenol is often formed as a by-product in the rearrangement of phenolic esters in the presence of aluminium chloride (cf. Cox, *J. Amer. Chem. Soc.*, 1930, **52**, 352). The action of benzoyl chloride on 4-methoxydiphenyl (IV) in the presence of aluminium chloride, under the conditions of Blicke and Weinkauff, also gives rise to two products, namely, *4-methoxy-4′-benzoyldiphenyl* (V) (m. p. 166°), probably identical with the sole product of Blicke and Weinkauff, and a second compound which is regarded as *4-methoxy-3 : 4′-dibenzoyldiphenyl* (m. p. 170°).

The identity of the 4-methoxy-3-benzoyldiphenyl (III), and hence of the corresponding hydroxy-compound (II) obtained from the Fries rearrangement, was established by its synthesis in two ways: (1) Bromination of 4-hydroxydiphenyl yielded 3-bromo-4-hydroxydiphenyl (VI) (Bell and Robinson, J., 1927, 1132), which was converted into 3-bromo-4-methoxydiphenyl (VII); the Grignard compound prepared from this, treated with benzaldehyde, gave a secondary alcohol (VIII), which on oxidation yielded 4-methoxy-3-benzoyldiphenyl (III). (2) Application of the Reimer–Tiemann reaction to 4-hydroxydiphenyl gave 4-hydroxy-3-aldehydodiphenyl (IX) (cf. Bell and Kenyon, J., 1926, 3044), from which 3-*aldehydo*-4-*methoxydiphenyl* (X) was obtained on methylation; addition of the methoxy-aldehyde to an ethereal solution of phenylmagnesium bromide led to the secondary alcohol (VIII), which on oxidation gave 4-methoxy-3-benzoyldiphenyl (III).

The identity of the 4-methoxy-4'-benzoyldiphenyl (V) obtained by the action of benzoyl chloride on 4-methoxydiphenyl in the presence of aluminium chloride could not be established in a similar way, because neither 4'-bromo- nor 4'-iodo-4-methoxydiphenyl could be induced to react with magnesium. However, nitration of 4-benzoyldiphenyl (XI) gave 4-*nitro*-4'-*benzoyldiphenyl* (XII), the position of the nitro-group in which was proved (a) by oxidation to *p*-nitrobenzoic acid and (b) by contrast with 4-p-*nitrobenzoyldiphenyl* and with 4-m-*nitrobenzoyldiphenyl*, prepared from the appropriate nitrobenzoyl chloride and diphenyl in the presence of aluminium chloride. Reduction of 4-nitro-4'-benzoyldiphenyl yielded 4-*amino*-4'-*benzoyldiphenyl* (XIII), which was converted successively into 4-hydroxy-4'-benzoyldiphenyl (XIV) and 4-methoxy-4'-benzoyldiphenyl (V).



EXPERIMENTAL.

4-Hydroxydiphenyl (m. p. 165°) was purchased or prepared either by the method of Norris, Macintire, and Corse (*Amer. Chem. J.*, 1903, 29, 120) or from 4-aminodiphenyl by means of the diazo-reaction (cf. Raiford and Colbert, *J. Amer. Chem. Soc.*, 1925, 47, 1456). Benzoylation

was effected either by Blicke and Weinkauff's method (*loc. cit.*) or by the usual Schotten–Baumann process. The benzoate crystallised from absolute alcohol in white needles, m. p. 150—151° (cf. Raiford and Colbert, *loc. cit.*; Kaiser, *Annalen*, 1890, **257**, 101).

Action of Aluminium Chloride on 4-Benzoyloxydiphenyl.—The following is typical of several experiments carried out under the conditions of Blicke and Weinkauff (*loc. cit.*). A solution of 4-benzoyloxydiphenyl (25 g.) in dry tetrachloroethane (125 c.c.) was heated with aluminium chloride (15 g.) at 140° (oil-bath) for 1 hour. The cold product was treated with ice and hydrochloric acid and distilled with steam to remove tetrachloroethane. The residue was extracted several times with hot aqueous sodium hydroxide and the solid precipitated on acidification of the filtered extract was dried and extracted with hot benzene. A little tar was removed by addition of ligroin. Concentration of the benzene solution deposited some 4-hydroxydiphenyl (m. p. and mixed m. p. 165° after crystallisation from aqueous alcohol). Further evaporation yielded an oily residue, which solidified on trituration with light petroleum (b. p. 40—60°). Repeated crystallisation from 95% alcohol gave 4-*hydroxy*-3-*benzoyldiphenyl* (II) in yellow needles, m. p. 89° (Found: C, 83·3; H, 5·5. $C_{19}H_{14}O_2$ requires C, 83·2; H, 5·1%). No trace of an alkali-soluble product, m. p. 193—195°, as claimed by Blicke and Weinkauff, could be detected. The *benzoyl* derivative, prepared by the Schotten–Baumann method, crystallised from aqueous alcohol in white needles, m. p. 95—96° (Found: C, 82·8; H, 5·05. $C_{26}H_{18}O_3$ requires C, 82·5; H, 4·8%). The *acetyl* derivative, obtained from the hydroxy-ketone (1 g.), acetic anhydride (5·6 g.), and anhydrous sodium acetate (3·8 g.) at 180—190° and crystallised from light petroleum (b. p. 40—60°), melted at 136—137° (Found: C, 79·9; H, 5·0. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·1%).

4-*Methoxy*-3-*benzoyldiphenyl* (III).—To a boiling solution of 4-hydroxy-3-benzoyldiphenyl (0·5 g.) in alcoholic potassium hydroxide (0·8 g. in the least quantity of absolute alcohol), an excess of methyl iodide was added in portions. When the colour was discharged (3 hours), the bulk of the solvent was evaporated, and water added to the residue, which was then extracted with ether. Removal of the ether from the dried extract left an oil which solidified. Recrystallisation from light petroleum (b. p. 60—80°) gave 4-*methoxy*-3-*benzoyldiphenyl* (III) in colourless transparent blades, m. p. 93° (Found: C, 83·2; H, 5·5. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·55%). The 2 : 4-*dinitrophenylhydrazone*, prepared by Brady's method (J., 1931, 756), separated from ethyl acetate in small orange-red crystals, m. p. 218—219° (Found: N, 12·1. $C_{26}H_{20}O_5N_4$ requires N, 12·0%).

Action of Benzoyl Chloride on 4-*Methoxydiphenyl in Presence of Aluminium Chloride* (cf. Blicke and Weinkauff, *loc. cit.*).—Benzoyl chloride (7 g.) was added gradually to a solution of 4-methoxydiphenyl (9 g., m. p. 88—89°; prepared by Werner and Rekner's method, *Annalen*, 1902, **322**, 167) in carbon disulphide (40 c.c.) to which finely powdered aluminium chloride (8 g.) had been added. After 24 hours the carbon disulphide was decanted from the brown viscous layer, ice and hydrochloric acid added, the mixture extracted with benzene, and the extract washed with aqueous sodium hydroxide and with water, dried, and evaporated. The residual oil after solidifying was fractionally crystallised from benzene–light petroleum (b. p. 60—80°), giving (a) 4-*methoxy*-4′-*benzoyldiphenyl* (V) in colourless needles, m. p. 166° (Found: C, 83·2; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·55%), and (b) colourless needles, m. p. 170°, regarded as 4-*methoxy*-3 : 4′-*dibenzoyldiphenyl* (Found: C, 82·9; H, 4·9. $C_{27}H_{20}O_3$ requires C, 82·6; H, 5·1%). The 2 : 4-*dinitrophenylhydrazone* of the former, prepared by Brady's method, separated from ethyl acetate in small red crystals, m. p. 221° (Found: N, 11·65. $C_{26}H_{20}O_5N_4$ requires N, 12·0%). Treatment of the product (b) in a similar manner yielded a 2 : 4-*dinitrophenylhydrazone* which separated from ethyl acetate in small red crystals, m. p. 221° (Found: N, 9·9. $C_{33}H_{24}O_6N_4$ requires N, 9·8%). The two hydrazones, and also the two parent compounds, depressed each other's m. p.

Synthesis of 4-*Methoxy*-3-*benzoyldiphenyl* (III).—(a) A solution of 3-bromo-4-hydroxydiphenyl (VI) (10 g.) (Bell and Robinson, J., 1927, 1132) in 10% aqueous sodium hydroxide (20 c.c.) was shaken with methyl sulphate (6·3 g.), diluted with water (20 c.c.), and, after ½ hour, heated on the steam-bath for 15 minutes. The granular solid which separated on cooling yielded 3-bromo-4-methoxydiphenyl (VII), m. p. 76—77° (from alcohol) (cf. Bell, J., 1930, 1075). To the Grignard solution prepared smoothly at 30° from 3-bromo-4-methoxydiphenyl (7·5 g.) and magnesium (0·7 g.) in dry ether (100 c.c.), benzaldehyde (3 g.) in dry ether was added gradually, and the mixture was finally boiled under reflux for ½ hour. After addition of ice and dilute sulphuric acid, the ethereal layer was separated, dried, and evaporated, leaving a viscous oil (9 g.), from which, on trituration with absolute alcohol, unchanged 3-bromo-4-methoxydiphenyl separated. The residual secondary alcohol (VIII) (5 g.) was added slowly to a stirred

mixture of potassium dichromate (7·5 g.), concentrated sulphuric acid (6 c.c.), and water (38 c.c.) and after 2 hours the temperature was raised to 40—50° for ½ hour. The mixture was diluted with water and extracted with ether, and the extract washed with dilute alkali solution to remove a little benzoic acid, and dried. The viscous residue obtained on removal of the solvent solidified on long standing and, after trituration with light petroleum (b. p. 40—60°), the product was crystallised from light petroleum (b. p. 60—80°). 4-Methoxy-3-benzoyldiphenyl (III) was obtained in colourless needles, m. p. 93° alone and on admixture with the compound obtained on methylation of the product of the Fries rearrangement of 4-benzoyloxydiphenyl.

(b) A mixture of 4-hydroxy-3-aldehydodiphenyl (IX) (6 g.) (Bell and Kenyon, J., 1926, 3047), powdered potassium hydroxide (11·5 g.), and absolute alcohol (150 c.c.) was boiled under reflux with the periodic addition of methyl iodide. After 10 hours the mixture was poured into water, and the precipitated solid extracted with ether. Acidification of the aqueous layer precipitated some unchanged 4-hydroxy-3-aldehydodiphenyl. The solid residue obtained on evaporation of the dried ethereal extract, after crystallisation from light petroleum (b. p. 60—80°), gave 3-*aldehydo*-4-*methoxydiphenyl* (X) in pale yellow needles, m. p. 79° (Found: C, 79·2; H, 5·7. $C_{14}H_{12}O_2$ requires C, 79·25; H, 5·7%). A solution of the methoxy-aldehyde (0·6 g.) in dry ether was added slowly to an ethereal solution of phenylmagnesium bromide prepared from bromobenzene (2 g.) and magnesium (0·3 g.) in dry ether (25 c.c.). Reaction was completed by heating on the water-bath for ½ hour. After addition of ice and dilute sulphuric acid, the ethereal layer was separated, dried, and evaporated, leaving the crude secondary alcohol (VIII) as a yellow viscous oil (1·5 g.), which on oxidation with dichromate mixture yielded 4-methoxy-3-benzoyldiphenyl (III), m. p. and mixed m. p. 93°.

Synthesis of 4-*Methoxy*-4′-*benzoyldiphenyl* (V).—4-Benzoyldiphenyl (XI) was prepared by the action of benzoyl chloride (50 g.) on a solution of diphenyl (27·5 g.) in benzene (65 c.c.) in presence of aluminium chloride (38·5 g.) (cf. Grieve and Hey, J., 1933, 970). One crystallisation from benzene-ligroin yielded 4-benzoyldiphenyl (35 g.), m. p. 100—102°, and distillation of the mother-liquor yielded benzophenone (cf. Montagne, *Rec. trav. chim.*, 1908, **27**, 357). Finely powdered 4-benzoydiphenyl (5 g.) was added in portions to well-stirred nitric acid (*d* 1·46; 100 c.c.) at 0—5° (cf. Grieve and Hey, *loc. cit.*). After 15 minutes the nitrating mixture, containing suspended solid, was poured into water and the precipitated product was crystallised several times from absolute alcohol, from which 4-*nitro*-4′-*benzoyldiphenyl* (XII) separated in pale yellow needles m. p. 154—156° (Found: N, 4·8. $C_{19}H_{13}O_3N$ requires N, 4·6%) (cf. I.G., E.P. 390556 and F.P. 735846). A portion of the nitro-compound (1 g.) was oxidised with chromic anhydride (5 g.) in boiling acetic acid (15 c.c.). After dilution with water, ether extracted *p*-nitrobenzoic acid (m. p. and mixed m. p. 238°). Powdered 4-nitro-4′-benzoyldiphenyl (5 g.) was added gradually to a hot solution of stannous chloride (18 g.) in concentrated hydrochloric acid (25 c.c.) and heating was continued for 1 hour on the steam-bath (cf. Gabriel and Stelzner, *Ber.*, 1896, **29**, 1303). The double salt, which separated when cold, was suspended in water and decomposed with an excess of sodium hydroxide. The liberated base was extracted with benzene and dried. Removal of the solvent left a solid residue (3 g.), which, on crystallisation from aqueous alcohol, gave 4-*amino*-4′-*benzoyldiphenyl* (XIII) in yellow blades, m. p. 143—144° (Found: N, 5·4. $C_{19}H_{15}ON$ requires N, 5·1%). Treatment with acetic anhydride yielded 4-*acetamido*-4′-*benzoyldiphenyl*, which separated from alcohol in white needles, m. p. 206—207° (Found: N, 4·5. $C_{21}H_{17}O_2N$ requires N, 4·4%). An ice-cold suspension of 4-amino-4′-benzoyldiphenyl (2·8 g.) in dilute sulphuric acid (*d* 1·4; 20 c.c.) was diazotised with aqueous sodium nitrite (0·8 g. in 5 c.c.) and the mixture was kept at room temperature for 1 hour, heated on the steam-bath, made alkaline with aqueous sodium hydroxide, filtered hot, and acidified. The precipitated product was extracted with benzene, evaporation of which yielded 4-hydroxy-4′-benzoyldiphenyl (XIV) (1 g.), which separated from benzene-light petroleum (b. p. 40—60°) in faintly yellow, translucent leaves, m. p. 195° (cf. Blicke and Weinkauff, *loc. cit.*). The 4-hydroxy-4′-benzoyldiphenyl (0·4 g.) was shaken with methyl sulphate (0·8 g.) and 5% aqueous sodium hydroxide (5 c.c.) and finally heated for 15 minutes on the steam-bath; the solid which separated on cooling, recrystallised from absolute alcohol, gave 4-methoxy-4′-benzoyldiphenyl (V) in white leaflets, m. p. 166° alone and on admixture with the product obtained from the action of benzoyl chloride on 4-methoxydiphenyl in the presence of aluminium chloride.

4-p-*Nitrobenzoyldiphenyl*.—A concentrated solution of *p*-nitrobenzoyl chloride (100 g.) in benzene was added in portions to a solution of diphenyl (35 g.) in the least quantity of benzene required for solution in the presence of powdered aluminium chloride (49 g.); the viscous product had to be warmed on the steam-bath before the addition was complete. When evolution of hydrogen chloride ceased, the mixture was treated with ice and the product was separated

in benzene from insoluble brown material, dried, recovered (25 g.), and crystallised from benzene-light petroleum (b. p. 40—60°), 4-p-*nitrobenzoyldiphenyl* separating in pale yellow needles, m. p. 165° (Found: N, 4·8. $C_{19}H_{13}O_3N$ requires N, 4·6%).

4-m-*Nitrobenzoyldiphenyl* (12 g. crude), prepared similarly from *m*-nitrobenzoyl chloride (25 g.), diphenyl (9 g.), benzene (45 c.c.), and aluminium chloride (12 g.), separated from absolute alcohol in white nacreous leaves, m. p. 130° (Found: N, 4·7%) (cf. Dilthey *et al.*, *J. pr. Chem.*, 1931, **129**, 189).

4-*Bromo- and* 4-*Iodo*-4'-*methoxydiphenyl*.—Since difficulty was experienced in obtaining a sufficient quantity of 4-bromo-4'-methoxydiphenyl by bromination of 4-methoxydiphenyl by Bell's method (J., 1930, 1075), an alternative process was adopted. 4-Nitrodiphenyl was brominated, and the resulting 4-bromo-4'-nitrodiphenyl reduced to the amino-compound (Le Fèvre and Turner, J., 1926, 2045), which was converted into 4-bromo-4'-hydroxydiphenyl (Bell and Robinson, J., 1927, 1131). Methylation with methyl sulphate and aqueous sodium hydroxide yielded 4-bromo-4'-methoxydiphenyl, which separated from alcohol in white blades, m. p. 144° (cf. Bell, *loc. cit.*). 4-Iodo-4'-aminodiphenyl was obtained (a) from diazotised benzidine and aqueous potassium iodide (Täuber, *Ber.*, 1894, **27**, 2627; Gelmo, *Ber.*, 1906, **39**, 4179), and (b) from the reduction of 4-iodo-4'-nitrodiphenyl, m. p. 210—211°, prepared by the method of Guglialmelli and Franco (*Anal. Asoc. Quím. Argentina*, 1931, **19**, 5), who record m. p. 202—206°. The reduction, effected by the method used by Le Fèvre and Turner (*loc. cit.*) for the corresponding bromo-compound, gave 4-iodo-4'-aminodiphenyl (85% yield), which separated from alcohol in white leaflets, m. p. 166° (cf. Guglialmelli and Franco, *loc. cit.*; Kawai, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1930, **13**, 260). 4-Iodo-4'-hydroxydiphenyl (m. p. 193°) was prepared from diazotised 4-iodo-4'-aminodiphenyl (cf. van Alphen, *Rec. trav. chim.*, 1931, **50**, 1111; Angeletti and Gatti, *Gazzetta*, 1928, **58**, 630) and methylated with methyl sulphate and aqueous sodium hydroxide. 4-Iodo-4'-methoxydiphenyl crystallised from benzene in white leaflets, m. p. 183°.

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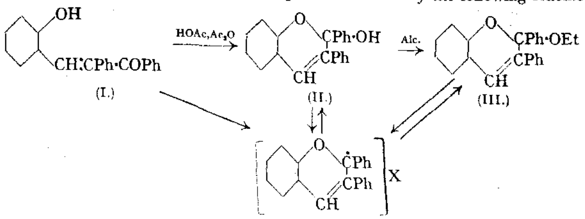
185. *The Condensation of Deoxybenzoin with Aromatic Aldehydes and Ketones. Part I. Condensation with Salicylaldehyde.*

By DOUGLAS W. HILL.

IT is well known that deoxybenzoin condenses with aromatic aldehydes in the presence of both acidic and alkaline reagents (Japp and Klingemann, *Ber.*, 1888, **21**, 2934; Knoevenagel and Weissgerber, *Ber.*, 1893, **26**, 436; Klingemann, *Annalen*, 1893, **275**, 50; Stobbe and Wilson, *ibid.*, 1910, **374**, 237; Das and Ghosh, J., 1919, **115**, 817; Singh and Mazumdar, *ibid.*, p. 821). With salicylaldehyde, however, condensation has hitherto only been effected in acids, with the formation of 3-phenylflavylium salts (Decker and Fellenberg, *Annalen*, 1909, **364**, 34; Gomberg and Cone, *ibid.*, 1909, **370**, 197; Das and Ghosh, *loc. cit.*; Singh and Mazumdar, *loc. cit.*; Löwenbein and Rosenbaum, *Annalen*, 1926, **448**, 223). It has now been achieved by alcoholic piperidine, after attempts with potassium hydroxide, sodium ethoxide, or diethylamine (cf. J., 1934, 1255; 1935, 1115; 1936, 256) had failed. The product was at first believed to be the dideoxybenzoin, but its reactions and molecular weight showed it to be *salicylidenedeoxybenzoin* (I). It does not agree in any way with Singh and Mazumdar's compound of the same name, m. p. 160° (*loc. cit.*). It does not behave as a typical chalkone. Although it is converted into 3-phenylflavylium chloride (separated as the ferrichloride) by hydrogen chloride in acetic acid in the normal manner, treatment with acetic anhydride or acetic acid produces 2 : 3-diphenylbenzo-2-pyranol (II), which is converted into the ethyl ether (III) by crystallisation from alcohol (compare Hill and Melhuish, J., 1935, 1161).

Contrary to Singh and Mazumdar's statement (*loc. cit.*), refluxing 3-phenylflavylium ferrichloride with alcoholic potassium hydroxide produces, not salicylidenedeoxybenzoin, but the pyranol ethyl ether (III).

The inter-relationship of the above compounds is shown by the following scheme :



EXPERIMENTAL.

Salicylidenedeoxybenzoin.—A solution of salicylaldehyde (5 c.c.) and deoxybenzoin (5 g.) in alcohol (50 c.c.) containing piperidine (5 c.c.) was kept for 3 days and poured into water (1 l.). When the precipitated oil solidified, the water was decanted, and the solid taken up in alcohol. The deep brown solution deposited pale brown crystals, which on recrystallisation from alcohol separated in almost colourless rhombs (2·5 g.), m.p. 129° [Found : C, 83·9; H, 5·6; *M* (Menzies–Wright), 312. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%; *M*, 300].

Conversion into 3-Phenylflavylium Ferrichloride.—(a) Hydrogen chloride was rapidly passed through a solution of the above ketone (1 g.) in glacial acetic acid (10 c.c.) for 5 minutes with cooling, and the orange-yellow solution then treated with ferric chloride (0·5 g.) in glacial acetic acid (7 c.c.). The yellow crystals of the ferrichloride were separated after an hour, washed with dry ether, and recrystallised from acetic acid; m. p. 123—124° (Decker and Fellenberg, *loc. cit.*, give m. p. 123—124°).

(b) The ketone (2 g.) in acetic anhydride (30 c.c.) was cooled and stirred during the addition of ferric chloride (1·5 g.) in 20% hydrochloric acid (7 c.c.) so that the temperature did not rise above 30°. After an hour the product was collected and recrystallised from glacial acetic acid, forming yellow needles, m. p. and mixed m. p. 123°.

Action of Acetic Anhydride or Glacial Acetic Acid on Salicylidenedeoxybenzoin.—The ketone (1 g.) was stirred at room temperature for 1½ hours or refluxed with acetic anhydride (20 c.c.), and the solution poured into water. The white precipitate crystallised from aqueous alcohol in small, hard, colourless cubes, m. p. and mixed m. p. with authentic 2 : 3-diphenylbenzo-2-pyranol ethyl ether 78—79°.

The ketone (2 g.) was refluxed in glacial acetic acid (30 c.c.) for 10 minutes and poured into water. A portion of the white flocculent precipitate, crystallised from light petroleum (b. p. 60—80°), gave colourless hard crystals of the pyranol, m. p. 125°. Another portion, crystallised from alcohol, gave the ethyl ether, m. p. 80°.

Action of Alcoholic Potassium Hydroxide on 3-Phenylflavylium Ferrichloride.—The ferrichloride (3 g.) was refluxed with 10% alcoholic potassium hydroxide (130 c.c.) for 3 hours, the filtered solution poured into water (500 c.c.), and the precipitate crystallised from alcohol, giving colourless crystals, m. p. and mixed m. p. with 2 : 3-diphenylbenzo-2-pyranol ethyl ether, 79°.

3-Phenylflavylium Chloride.—Hydrogen chloride was passed through a solution of deoxybenzoin (5 g.) and salicylaldehyde (3 g.) in dry ether for 2 hours with cooling, and again for 1 hour after an interval of 24 hours. The long orange needles of the flavylium chloride were collected, washed with dry ether, and dried over calcium chloride in a vacuum desiccator; they darkened at 110—115° and had m. p. 158° (decomp.) (Found : C, 70·7; H, 4·7; Cl, 18·4. Calc. for $C_{21}H_{16}OCl_2$: C, 70·9; H, 4·6; Cl, 19·9%). Gomberg and Cone (*loc. cit.*) describe the salt as a dichloride crystallising in yellow needles (contrast Das and Ghosh; Singh and Mazumdar, *locc. cit.*).

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186. *Molecular Dissymmetry due to symmetrically placed Hydrogen and Deuterium. Part I. The Resolution of α-Pentadeuterophenylbenzylamine.*

By G. R. Clemo and (the late) A. McQuillen.

The preparation of organic compounds containing deuterium has rendered possible an examination of the very intriguing possibility of optical activity due to dissymmetry arising from the difference between hydrogen and deuterium. We have been engaged on the question for nearly a year, and in view of the failure of Gärtner and Erlenmeyer (*Helv. Chim. Acta*, 1936, **19**, 331) to obtain evidence of dissymmetry in one case, we think it advisable to place on record work proving that resolution of such compounds is possible.

According to the theory of Boys (*Proc. Roy. Soc.*, 1934, *A*, **144**, 655), such activity might be expected to be small, and our results might be taken to confirm this. No calculation of the extent of the activity from the theoretical views of Werner, Kuhn, and Born has yet been made on account of the lack of certain physical data. The actual preparation of a suitable compound of the type CXYHD is no easy matter and after considering various possibilities we decided to examine α-pentadeuterophenylbenzylamine (II). The main reason for this choice was the hope that a compound containing phenyl and pentadeuterophenyl would give a greater activity than one in which the dissymmetry was due to single atoms of hydrogen and deuterium.

Pentadeuterobenzophenone (I) was prepared from hexadeuterobenzene (J., 1935, 851) and benzoyl chloride by the Friedel–Crafts reaction. Although this reaction may be

(I.) $C_6D_5{\cdot}CO{\cdot}C_6H_5$ $C_6D_5{\cdot}CH(NH_2){\cdot}C_6H_5$ (II.)

criticised on account of the reported interchanges, (i) $C_6H_6 + 6DCl \xrightleftharpoons{Al_2Cl_6} C_6D_6 + 6HCl$ (Klit and Langseth, *Nature*, 1935, 956) and (ii) $C_6D_6 + Cl{\cdot}CO{\cdot}NH_2 \xrightarrow{Al_2Cl_6} C_6D_3H_2{\cdot}CO{\cdot}NH_2$ (Erlenmeyer, *loc. cit.*, p. 337), the experimental conditions were arranged to expedite the removal of the evolved deuterium chloride and the analytical data prove that the deuterium content was unaltered. The exchange of deuterium and hydrogen in balanced amounts between the two benzene nuclei is much less likely to occur; nevertheless this problem is being investigated by the examination of the Beckmann transformation of pentadeuterobenzophenoneoxime. This compound was reduced in alkaline solution to the amine (II) and the base was resolved by fractional crystallisation of its d- and l-*hydrogen tartrates*, the specific rotations of which reached constant values of $\pm$ 13·2° after some ten recrystallisations from ethyl alcohol and light petroleum mixtures. The oxalates of the *d*- and *l*-bases obtained from these salts only displayed the low activity of $\alpha \pm 0{\cdot}02°$, corresponding to $[\alpha]_D - 2{\cdot}5°$ for the *oxalate* obtained from the d-*tartrate* and + 2·2° for the enantiomorphous form. In this connection it should be noted that in the case of α-phenylethylamine the less soluble tartrates formed are the *d*-base *l*-tartrate and the *l*-base *d*-tartrate. In view of the fact that salts of α-phenylethylamine show much lower activities than the base itself, we determined the rotation of the free base (II) in alcohol with the aid of a micropolarimeter tube and found $\alpha - 0{\cdot}136°$ and $+ 0{\cdot}041°$ for 4·77% and 1·64% solutions. This gives $[\alpha]_D^{16°} - 5{\cdot}7°$ and + 5·0° respectively.

Further work in this field is in progress. As the necessary lens system to get the best results from the use of the micropolarimeter tube cannot be obtained for a considerable time, we now lay claim to have proved the resolvability of the base (II), rather than to have obtained its actual specific rotation to a high degree of accuracy.

Experimental.

Pentadeuterobenzophenone (I).—Hexadeuterobenzene (0·6 g.) was placed in a small flask (3 c.c.) fitted with a short ground-in condenser tube cooled at the bottom by a water condenser and at the top by a jacket containing solid carbon dioxide. Carbon disulphide (1 c.c.) and finely powdered aluminium chloride (0·75 g.) were added, and the whole cooled in solid carbon dioxide.

Benzoyl chloride (0·8 g.) was added, the condenser attached, and the mixture refluxed for 12 hours, a trap containing caustic potash being attached directly to the condenser tube to remove the evolved deuterium chloride. The product was decomposed by boiling with water (5 c.c.) and hydrochloric acid (1 c.c.) and extracted with ether; the extract was washed with dilute caustic soda solution and water and dried over sodium sulphate. After removal of the ether, pentadeuterobenzophenone (0·95 g.) distilled at 160°/15 mm.

Pentadeuterobenzophenoneoxime.—Pentadeuterobenzophenone (0·95 g.) in alcohol (9 c.c.) was refluxed for 2 hours on the water-bath with hydroxylamine hydrochloride (1·1 g.) in water (2·7 c.c.) and caustic potash (1·8 g.) in water (2·7 c.c.). After pouring into water (12 c.c.) and acidification with dilute sulphuric acid, the *oxime* (0·95 g.) was filtered off and recrystallised from alcohol; m. p. 140°, undepressed by benzophenoneoxime (Found : C, 77·0; water, 48·4. $C_{13}H_6D_5ON$ requires C, 77·2; water, 51·4%).

α-Pentadeuterophenylbenzylamine (II).—Pentadeuterobenzophenoneoxime (0·95 g.) was reduced in dilute alkaline solution by heating for 6 hours on the water-bath with 4% sodium amalgam (150 g.), dilute acetic acid being added occasionally to diminish the concentration of alkali. The base was extracted with ether (five extractions), and the ethereal solution dried over sodium sulphate. After removal of the ether the free base (0·89 g.) was obtained as a yellow oil, which rapidly absorbed carbon dioxide.

Resolution.—l-*α-Pentadeuterophenylbenzylamine* d-*hydrogen tartrate.* Pentadeuterophenylbenzylamine (0·89 g.) was converted into the d-*hydrogen tartrate* by addition of an aqueous solution of *d*-tartaric acid (0·7 g.) and evaporation to dryness. This acid tartrate (1·2 g.), recrystallised from alcohol–light petroleum, formed fine needles, m. p. 181° (Found : C, 60·3; water, 52·0. $C_{13}H_8D_5N,C_4H_6O_6$ requires C, 60·3; water, 52·1%. $C_{13}H_{13}N,C_4H_6O_6$ requires C, 61·3; water, 51·4%). On further recrystallisation the specific rotation increased regularly from + 10·8° to a limiting value of + 13·2° for l-*α-pentadeuterophenylbenzylamine* d-*hydrogen tartrate*, m. p. 181° (Found : C, 60·4; water, 55·2%).

d-*α-Pentadeuterophenylbenzylamine* l-*hydrogen tartrate.* From the collected mother-liquors, the corresponding salt with *l*-tartaric acid was prepared. The l-*hydrogen tartrate* (0·65 g.), m. p. 181°, was recrystallised from alcohol–petroleum until the constant value of $[\alpha]_D$ − 13·2° was obtained (Found : C, 60·5; water, 53·9%).

No. of recrystns.	3	4	7	8	9	10
Substance, g.	0·92	0·85	0·44	0·348	0·270	0·265
$[\alpha]_D$	+10·8°	+11·3°	+12·6°	+13·0°	+13·3°	+13·2°

No. of recrystns.	3	5	9	11	13
Substance, g.	0·29	0·25	0·21	0·14	0·088
$[\alpha]_D$	−10·4°	−10·5°	−11·3°	−13·4°	−13·1°

l-*α-Pentadeuterophenylbenzylamine Oxalate.*—*l*-Pentadeuterophenylbenzylamine *d*-hydrogen tartrate (0·27 g.) was shaken with caustic soda solution, an ethereal extract of the base washed with alkali and water and dried over sodium sulphate, and the ether removed through a fractionating column, leaving the base (0·16 g.); this was treated with an aqueous solution of oxalic acid (0·06 g. of the dihydrate), giving the normal *oxalate* (0·16 g.) which, recrystallised from water, formed needles, m. p. 204°; mixed with benzhydrylamine oxalate, m.p. 205° (Found : C, 72·1; water, 54·7. $2C_{13}H_8D_5N,C_2H_2O_4$ requires C, 72·1; water, 56·2%). Approximately 0·4% alcoholic solutions of this oxalate gave α − 0·023°, − 0·017°, and − 0·024°, corresponding to $[\alpha]_D^{17°}$ − 2·6°, − 2·4°, and − 2·5° respectively. The mean deviation from the mean for a series of sixty observed readings was 0·006°.

d-*α-Pentadeuterophenylbenzylamine Oxalate.*—The corresponding oxalate from the *d*-pentadeuterophenylbenzylamine *l*-hydrogen tartrate ($[\alpha]_D$ − 13·3°) gave values of + 0·013° and + 0·015°, corresponding to $[\alpha]_D^{16°}$ + 1·9° and + 2·2°. The mean deviation from the mean was 0·005°.

l-*α-Pentadeuterophenylbenzylamine.*—*l*-Pentadeuterophenylbenzylamine oxalate ($[\alpha]_D$ − 2·5°) was converted into the free base. About 10 mg. of this amine and about 0·25 c.c. of alcohol were weighed accurately into a small weighing-bottle by means of a microbalance. The density of the solution was determined with a micropyknometer (J., 1935, 1220), and hence the concentration of the base calculated. A micropolarimeter tube, 5 cm. in length, was filled with the solution and values for α of − 0·14° observed, giving $[\alpha]_D^{19°}$ − 5·7° for the free base in a 4·77% solution in alcohol. The mean deviation from the mean of the readings was 0·010°.

d-*α-Pentadeuterophenylbenzylamine.*—*d*-Pentadeuterophenylbenzylamine oxalate (7 mg., $[\alpha]_D$ + 2·2°) was converted into the free base (5·5 mg.). A 1·64% solution of this amine in alcohol

gave observed rotations of 0·041°, giving a value for $[\alpha]_D^{16°} = +5{\cdot}0°$. The mean deviation from the mean over a series of twenty readings was 0·009°.

We are indebted to Imperial Chemical Industries, Ltd., for a grant, to Mr. O. Telfer for the analyses, and one of us (A. McQ.) to the Council of Armstrong College for a post-graduate Studentship.

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187. *Electrolytic Reduction of Organic Compounds. Part III. β-Vinylacrylic Acid.*

By ELIAS ISAACS and CHRISTOPHER L. WILSON.

ELECTROLYTIC reduction processes have been divided into two categories depending on the nature of the cathode; these are (1) spongy nickel and platinised platinum cathodes, at which the reduction is essentially of a catalytic nature, and (2) most other metallic cathodes which simulate the reducing properties commonly attributed to dissolving metals and metallic couples (this vol., pp. 202, 574).

Although these conclusions were based partly on the mode of reduction of sorbic acid under various conditions, they were considered to be generally applicable to unsaturated systems. We were therefore surprised by the results recorded by Muskat and Knapp * (*J. Amer. Chem. Soc.*, 1934, **56**, 943), who reduced β-vinylacrylic acid at a spongy nickel cathode and stated that, after the absorption of approximately 1 mol. of hydrogen, the product (in a maximum yield of 30%) was almost entirely Δ^{β}-*n*-pentenoic acid.

It has been established that the partial catalytic reduction of β-vinylacrylic acid in alcoholic solution under the influence of platinum-black produces mainly Δ^{α}-*n*-pentenoic acid and *n*-valeric acid (*idem*, *Ber.*, 1931, **64**, 779; Farmer and Galley, J., 1932, 130). Furthermore, sorbic acid, both by catalytic reduction and by electrolytic reduction at prepared nickel and platinum surfaces, gives a mixture containing much Δ^{α}-*n*-pentenoic acid and *n*-hexoic acid. We have therefore reinvestigated the electrolytic reduction of β-vinylacrylic acid, using as analytical procedure a combination of the halogen absorption method (which we have shown to be adaptable to the estimation of the pentenoic acids) and ozonolysis (this vol., p. 205).

Reduction Products of β-Vinylacrylic Acid.

Reducing agent.	Medium.	Yield of reduction product (%).	*n*-Pentenoic acids (%).		*n*-Valeric acid (%).	"Pinacol-like" polymeride (%).
Spongy nickel cathode	EtOH + NaCl	63	25·1 (Δ^{α})	55·4 ($\Delta^{\beta} + \Delta^{\gamma}$)	19·5	0
	N/2-NaOH	80	15·6 (,,)	34·9 (,,)	49·5	0
Copper cathode ...	*N*/2-NaOH	85	0	99·2 (Δ^{β})	0	0
Mercury cathode...	$NaHCO_3$	97	0	75·0 (,,)	0	25·0
Sodium amalgam *	$NaHCO_3$	—	0	80 (,,)	0	?

* Burton and Ingold, J., 1929, 2022.

In the experiment indicated by the first row of the table we have used the same solvent and cathode as employed by Muskat and Knapp (*loc. cit.*). Our product, however, contained Δ^{α}-*n*-pentenoic and *n*-valeric acids. Similar results were also obtained at a spongy nickel cathode in alkaline solution.

The three pentenoic acids have also been reduced at a prepared nickel cathode, and it has been shown that the relative ease of reduction of these acids and the parent butadiene acid follows a series, vinylacrylic $\gg \Delta^{\alpha}\text{-} > \Delta^{\beta}\text{-} > \Delta^{\gamma}$-*n*-pentenoic acid, in both acid and alkaline solution.

* These authors claim priority for the electrolytic reduction of a butadienoid system, but this was actually accomplished long ago (Mettler, *Ber.*, 1906, **39**, 2942).

Experiments with copper and mercury cathodes are also shown in the table, and the results clearly display the division of cathodes into the catalytic and non-catalytic classes. For comparison with data for the latter groups of cathodes, a result of Burton and Ingold's for amalgam reduction is included in the table. In these experiments loss of vinylacrylic acid can be accounted for by polymerisation, which most probably occurs during the isolation of the reduction product and not during the reduction itself (cf., however, *idem, ibid.*). When mercury is the active metal, a considerable proportion of the material is converted into pinacol-like dimeride.

On the whole, the results in the table given above are in excellent agreement with those obtained for sorbic acid (this vol., pp. 202, 574).

Muskat and Knapp (*loc. cit.*) have presented a classification of reducing agents, grouping them as follows: (1) reducing ions (*e.g.*, chromous chloride), (2) dissolving metals, and (3) catalytic agents. It was stated that in contrast with the course of catalytic hydrogenation, reagents of group (2) usually add hydrogen terminally to conjugated systems. As a consequence of their findings (already referred to on p. 810) in the reduction of vinylacrylic acid at a spongy nickel cathode, electrolytic methods of reduction were placed in group (2). This is partly true, since we have shown that metallic cathodes, other than prepared nickel and platinum, exhibit reducing properties analogous to dissolving metals, but the experimental basis upon which Muskat and Knapp's allocation was made was too superficial.

Experimental.

Materials.—β-Vinylacrylic acid was prepared by Kohler and Butler's modification (*J. Amer. Chem. Soc.*, 1926, **48**, 1041) of Döbner's method (*Ber.*, 1902, **35**, 1137). Crystallisation of the product from ether-petroleum (1 : 3) gave small colourless prisms, m. p. 77—78°, unchanged by recrystallisation. Δ^{α}-, Δ^{β}-, and Δ^{γ}-*n*-Pentenoic acids were prepared by standard methods (Linstead and collaborators, J., 1933, 574, 559, 582) and had b. p. respectively 102—103°/17 mm., 90—92°/14 mm., and 93°/20 mm.

Method.—The preparation of the cathodes, conditions of reduction, and isolation of the products were as previously described for sorbic acid (Isaacs and Wilson, *loc. cit.*). Under the conditions defined previously (*idem, ibid.*) all three pentenoic acids reacted quantitatively with bromine in 6 hrs., and addition of iodine to the Δ^{β}- and the Δ^{γ}-acid was complete in 12 hrs., after which period Δ^{α}-*n*-pentenoic acid had reacted to the extent of only 2%. For the isolated reduction product the bromine and iodine absorptions are represented by *B* (Δ^{α}- + Δ^{β}- + Δ^{γ}-*n*-pentenoic acids) and *J* (Δ^{β}- + Δ^{γ}-*n*-pentenoic acids) respectively.

Details of Reductions.—*Expt.* 1 (Muskat and Knapp's conditions). Vinylacrylic acid (10 g.) in ethyl alcohol (400 c.c., 95%) with saturated sodium chloride solution (20 c.c.) was reduced at spongy nickel by 0·5 amp. for 28 hrs. (theo. for 4H, 24 hrs.). The product consisted of (*a*) 6·3 g. of a colourless liquid, b. p. 97—98°/18 mm. (Found: *B*, 80·5; *J*, 55·4. Valeric acid, 19·5; Δ^{α}, 25·1; Δ^{β} + Δ^{γ}, 55·4%), and (*b*) 2·7 g. of residual polymeride which could not be distilled.

Expt. 2. *Nickel in alkaline solution.* Vinylacrylic acid (8 g.) in *N*/2-sodium hydroxide (500 c.c.), reduced by 18 amp.-hrs. of current (theo. for 4H, 10 amp.-hrs.), gave (*a*) 6·4 g. (80%) of a colourless liquid, b. p. 89—90°/13 mm. (Found: *B*, 50·5; *J*, 34·9. Valeric acid, 49·5; Δ^{α}, 15·6; Δ^{β} + Δ^{γ}, 34·9%), and (*b*) 0·6 g. undistillable residue. 5·1 G. of (*a*) after standing for 24 hrs. with excess bromine, were distilled, and gave a liquid, b. p. 90—91°/17 mm. (2·2 g.), identified as *n*-valeric acid by formation of the amide, m. p. 104·5° (Robertson, J., 1919, 1220, gives 106°) (Found: C, 59·1; H, 10·9; N, 13·4. Calc.: C, 59·3; H, 11·0; N, 13·8%).

Expt. 3. *Copper in alkaline solution.* 10 G. of the acid in *N*/2-sodium hydroxide (500 c.c.), after passage of 18 amp.-hrs. of current (theo. for 2H, 6 amp.-hrs.), gave (*a*) a liquid, b. p. 93—94°/16 mm. (8·5 g., 85%) (Found: *B*, 99·3; *J*, 99·2; Δ^{β} + Δ^{γ}, 99·2%), and (*b*) 0·7 g. of undistillable polymeride.

Ozonolysis of (*a*) (2·780 g.) in chloroform solution at 0° and decomposition of the ozonide with water gave, by passage of the evolved vapours through 2 : 4-dinitrophenylhydrazine in 2*N*-hydrochloric acid, 5·81 g. acetaldehyde-2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 162° (Found: C, 43·2; H, 3·6. Calc.: C, 42·9; H, 3·6%). This corresponds to 93·4% of Δ^{β}-pentenoic acid in (*a*) (Muskat and Knapp, *loc. cit.*, claimed a maximum yield of 87% of acetaldehyde from their "pentenoic" acid). The aqueous solution from the ozonide fission was refluxed for 2 hrs., hydrogen peroxide (40 c.c., 20-vol.) added, and the mixture left overnight. To a portion of this solution calcium acetate solution was added, but no oxalic acid was thereby

detected (Found : Δ^{α}, 0%). Evaporation of the remainder of the solution to dryness failed to indicate the presence of succinic acid (Found : Δ^{γ}, 0%) (cf. Burton and Ingold, *loc. cit.*).

Expt. 4. *Mercury in neutral solution.* Vinylacrylic acid (12 g.) was dissolved in sodium bicarbonate solution and electrolysed at 0·5 amp. for 18 amp.-hrs. (theo. for 2H, 7 amp.-hrs.) whilst a constant stream of carbon dioxide was passing through the catholyte. The product consisted of (*a*) 8·7 g. of a liquid, b. p. 93—94°/16 mm. (Found : *B*, 99·6; *J*, 99·8; $\Delta^{\beta} + \Delta^{\gamma}$, 99·6%), and (*b*) 2·6 g. of a light brown viscous liquid, b. p. 210—213°/16 mm. (slight decomp.), 170—172°/<1 mm. (analogous to the sorbic acid " pinacol ").

2·500 G. of (*a*) were ozonised as before, and gave 5·29 g. of acetaldehyde-2 : 4-dinitrophenylhydrazone, m. p. 161·5°, mixed m. p. 162° (Found : C, 42·9; H, 3·8%), corresponding to 94·5% of Δ^{β}-pentenoic acid. Addition of lead acetate solution to the aqueous solution from the ozonide fission gave a precipitate which was decomposed in aqueous suspension by hydrogen sulphide. Evaporation of the filtrate from the lead sulphide gave malonic acid, m. p. 132·5° (decomp.), mixed m. p. 133° (presence of Δ^{β}-pentenoic acid). The remainder of the solution from the ozonide fission after treatment with hydrogen peroxide gave no trace of succinic acid (Found : Δ^{γ}, 0%).

Relative Rates of Reduction.—By alternately placing equally concentrated solutions of unsaturated acids A and B in the reduction cell of the differential apparatus (Isaacs and Wilson, *loc. cit.*), it was possible to measure the amounts of hydrogen absorbed in the two cases. Successive values for the acid A differed slightly owing to progressive deterioration of the cathode, but the mean of two successive figures was compared with the intervening one for the acid B. In such a manner a quite definite and reproducible series was established (the subscripts 1 and 2 refer to 70% acetic acid and *N*/2-caustic soda solution respectively) :

$$\text{Vinylacrylic}_1 > \text{Vinylacrylic}_2 \gg \Delta^{\alpha}{}_1 > \Delta^{\alpha}{}_2 > \Delta^{\beta}{}_1 > \Delta^{\beta}{}_2 > \Delta^{\gamma}{}_1 > \Delta^{\gamma}{}_2.$$

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188. *The Detection of Reaction Chains by Small Amounts of Nitric Oxide. The Thermal Decomposition of Acetaldehyde and of Propaldehyde.*

By L. A. K. Staveley and C. N. Hinshelwood.

The rate of the homogeneous thermal decomposition of ethyl ether can be reduced to about one-third by the addition of amounts of nitric oxide of the order of a millimetre (Staveley and Hinshelwood, *Proc. Roy. Soc.*, 1936, *A*, **154**, 335; *Nature*, 1936, **137**, 29). This suggests that in the normal decomposition of ether, short chains are involved, which according to current ideas would be radical chains, and that nitric oxide breaks these by removing the free radicals from the system. Since only the average chain length is known, it has not so far been possible to decide whether dissociation of an activated ether molecule always yields radicals, giving chains of about three cycles, or whether only a few molecules give much longer chains. An upper limit to their length is set by the fact that the decomposition of ether has none of the characteristics associated with long chains.

While the inhibiting action of nitric oxide in organic decomposition reactions is not a general one, it is nevertheless not restricted to the single case of ethyl ether. The use of nitric oxide as a means of detecting short chains accordingly opens up two main fields of investigation. One is the detailed examination of the kinetics of typical reactions which are inhibited by nitric oxide, with the object of obtaining further information about their mechanism. The other is the systematic survey of different types of organic reaction in order to find which of these involve a chain mechanism, and to establish any connections between chain-length and molecular structure. Nitric oxide provides a definite quantitative test for the presence of chains, and absence of inhibition may be taken as evidence for their absence. This is shown by two facts : first, that different types of thermal reaction have their rates reduced, but only to definite limits, and, secondly, that nitric oxide reduces the

quantum yield in the photocatalytic decomposition of acetaldehyde from several hundred to nearly unity (Mitchell, unpublished observations).

The decomposition of propaldehyde shows inhibition by small amounts of nitric oxide, and as it has points of kinetic interest not found with ethyl ether, it was thought that detailed investigation might be profitable. The decomposition of acetaldehyde, however, is completely exempt from the inhibition. As the results obtained with propaldehyde provide a clue to the reasons for this different behaviour, the two substances will be treated together.

Experimental.

The apparatus and method used in the investigation were essentially the same as those previously employed.

As it has been found that the decomposition of aldehydes is strongly catalysed by small amounts of oxygen, the bulb containing the aldehyde was periodically cooled in a mixture of solid carbon dioxide and acetone and evacuated. Special precautions were taken throughout to avoid access of air.

The Influence of Small Amounts of Nitric Oxide on the Decomposition of Acetaldehyde.—The acetaldehyde used was carefully distilled in an all-glass apparatus (b. p. 20·4—21·0°).

That nitric oxide has no detectable inhibiting influence whatsoever on the decomposition of acetaldehyde is shown by Table I, where $t_{\frac{1}{2}}$ is the time required for 50% of the aldehyde to react.

Table I.

Influence of nitric oxide on the decomposition of acetaldehyde.

Temp. 559°. Initial pressure of aldehyde 150 mm.

NO (mm.)	0	0·11	0·53	1·0	5·5
$t_{\frac{1}{2}}$ (sec.)	173	174	172	165	132

The decomposition of acetaldehyde is positively catalysed by large amounts of nitric oxide (Verhoek, *Trans. Faraday Soc.*, 1935, **31**, 1533). It will be seen from Table I that even 5·5 mm. of nitric oxide noticeably increase the rate of decomposition.

The absence of inhibition shows a non-chain mechanism for the decomposition of acetaldehyde. Rice and Herzfeld (*J. Amer. Chem. Soc.*, 1934, **56**, 284) have suggested a chain mechanism with the following primary process : $CH_3·CHO \longrightarrow CH_3 + CHO$. The observed activation energy of the decomposition is between 55,500 and 47,700 cals., according to the initial pressure, whereas the above primary process would require about 70,000. To account for the observed reaction rate the chains would have to be very long. One would therefore expect to find the wall effects characteristic of long-chain reactions, but in reality at the temperatures in question these are entirely absent (*Proc. Roy. Soc.*, 1935, *A*, **149**, 355). The fact that the decomposition of acetaldehyde can be accelerated by the addition of azomethane has been taken to support the chain mechanism (Sickman and Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 1251), methyl radicals being assumed to be formed by the thermal decomposition of the azomethane, and to react with aldehyde molecules. It must be borne in mind, however, that the decomposition of acetaldehyde can also be catalysed by a number of very simple inorganic substances, such as iodine, hydrogen sulphide and nitric oxide. For the high-temperature photochemical reaction, Leermakers (*ibid.*, p. 1537) found a high quantum yield. The photochemical production of free radicals, which might in any case be expected, from what we know of other catalysts (Bairstow and Hinshelwood, *Proc. Roy. Soc.*, 1933, *A*, **142**, 77 ; Fromherz, *Z. physikal. Chem.*, 1934, *B*, **25**, 301 ; Hinshelwood, J., 1935, 1111), to have a catalytic action on the decomposition of acetaldehyde, does not prove their occurrence in the thermal reaction.

The Influence of Small Amounts of Nitric Oxide on the Decomposition of Propaldehyde.—The propaldehyde was fractionated in an all-glass apparatus ; b. p. 47·5—48·5°/730 mm.

The chief products of its thermal decomposition are carbon monoxide, ethane, methane, ethylene, and hydrogen. Winkler, Fletcher, and Hinshelwood (*Proc. Roy. Soc.*, 1934, *A*, **146**, 345) found that the end-point of the reaction increases as the initial pressure decreases. The decomposition of the ethane causes a further very slow pressure increase after the aldehyde has decomposed. Consequently, the true " end-points " were obtained from the pressure–time curves by an extrapolation process. The true end-points of the reaction in the presence of 2 mm. of nitric oxide were found in the same way, and do not differ much from those for the uninhibited reaction. This is shown by Table II.

TABLE II.

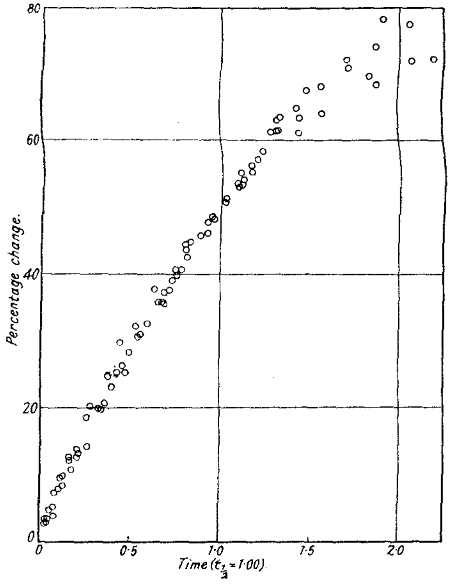
Propaldehyde (549°). *Variation of end-point with initial pressure.*

p_o = initial pressure, p_e = final pressure at true end-point.

		300	150	40	10
p_0		300	150	40	10
$(p_e - p_0)/p_0$	without NO	1·00	1·04	1·13	1·20
	with 2 mm. NO	1·03	1·05	1·13	1·19

As with ethyl ether, some nitric oxide is removed during the reaction, but the reciprocal of $t_{\frac{1}{2}}$ (the time required for 50% of the aldehyde to decompose) has been used as a measure of the

FIG. 1.



Nitric oxide-inhibited reaction of propaldehyde. Similarity of pressure–time curves for different conditions : seven curves, temperatures from 549° *to* 610°, *aldehyde pressures from* 11 *to* 301 *mm.*, NO *from* 0 *to* 9·4 *mm.*

rate in preference to the less accurately measurable initial rates, a procedure justified by th fact that the shape of the pressure–time curve is independent of the temperature and of aldehyd or nitric oxide pressure (as long as the latter is fairly small). This is shown by Fig. 1, in whic] are plotted the pressure–time curves for 7 runs carried out at various temperatures and pressure: $t_{\frac{1}{2}}$ in each case being made equal to unity.

Table III gives the values of $t_{\frac{1}{2}}$ at 549° with 159 mm. of aldehyde and amounts of nitri oxide varying from 0 to 18 mm. The relation between $1/t_{\frac{1}{2}}$ and nitric oxide pressure is illustrate in Fig. 2, which shows the reaction to be inhibited by nitric oxide, although the curve, unlik that for ethyl ether, has no long flat minimum, the positive catalytic influence of nitric oxid

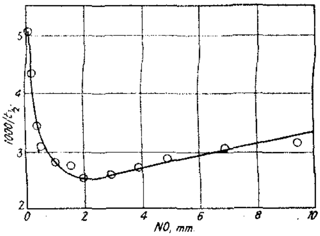
TABLE III.

Propaldehyde (549°). *Variation of* $t_{\frac{1}{2}}$ *with* NO *pressure.*

NO (mm.).	$t_{\frac{1}{2}}$ (sec.).	NO (mm.).	$t_{\frac{1}{2}}$ (sec.).	NO (mm.).	$t_{\frac{1}{2}}$ (sec.).
0	197	1·53	363	6·9	326
0·18	230	1·95	394	9·4	315
0·38	291	2·9	384	10·1	282
0·51	326	3·9	368	12·7	280
1·00	356	4·9	349	14·7	251

being considerably more pronounced. By extrapolating the rising part of the curve until it cuts the pressure axis, it can be seen that, if there were no concurrent catalysis, the minimum rate would be about 44% of that of the uninhibited reaction.

FIG. 2.

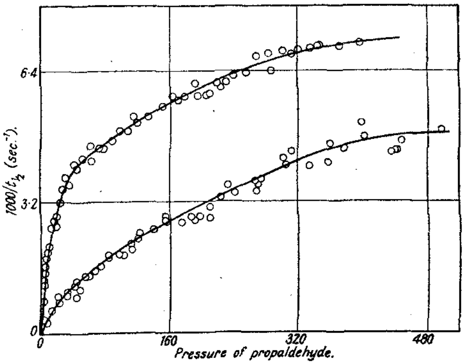


Decomposition of propaldehyde: inhibition by nitric oxide.

$t_{\frac{1}{2}}$ was determined at 549° with 2 mm. of nitric oxide and with initial aldehyde pressures varying from 5 to 500 mm. For pressures less than 40 mm., the reaction was followed with the aid of a cathetometer, which enabled the pressure to be read to 0·1 mm. The results are plotted in Fig. 3, together with those of Winkler, Fletcher, and Hinshelwood for the uninhibited reaction. The most striking thing about the figure is the parallelism between the two curves above about 40 mm., the chain length, as given by the ratio of the velocities of the uninhibited and the inhibited reaction, increasing as the pressure decreases. The interpretation of this is discussed later.

The energy of activation of the normal decomposition of propaldehyde increases as the initial pressure decreases. The temperature coefficient of the reaction inhibited by 2 mm. of nitric oxide was investigated at two different aldehyde pressures, *viz.*, 30 and 350 mm. The

FIG. 3.



Influence of nitric oxide on decomposition of propaldehyde at different initial pressures. Upper curve, normal reaction; lower curve, reaction with 2 *mm.* NO.

observed values of $t_{\frac{1}{2}}$ are corrected for change of concentration with temperature (Table IV). They give satisfactory Arrhenius lines.

TABLE IV.

Inhibited decomposition of propaldehyde. Temperature coefficient.

		606°	589°	569°	549°	529°	509°	489°
Temp.		606°	589°	569°	549°	529°	509°	489°
$\log_{10}t_{\frac{1}{2}}$	30 mm.	1·922	2·279	2·588	2·976	3·354	—	—
	350 mm.	—	—	1·982	2·356	2·697	3·064	3·398

The values for the activation energies (uncorrected for variation of the collision rate with temperature) are 58,500 cals. at 30 mm. and 51,000 cals. at 350 mm., so that, as for the uninhibited reaction, the activation energy increases as the initial pressure decreases. The corresponding values for the normal decomposition are 63,500 and 56,000 cals. respectively, *i.e.*, about 5,000 cals. greater than those for the inhibited decomposition. Thus the chains must get slightly longer as the temperature rises, whereas in the case of ethyl ether they get shorter.

DISCUSSION.

It is well known that if the rate of an organic decomposition reaction, as given by the reciprocal of the time of half-change, is plotted against the initial pressure, the curve rises from the origin, bends over, and ultimately becomes more or less parallel to the pressure axis. If in any given reaction there is only one type of activated molecule, then, theoretically, this curve should show a gradual change of slope and tend to become exactly parallel to the pressure axis at high pressures. The initial slope of the curve is proportional to the rate of production of activated molecules, and its limiting height to the probability of their decomposition. Closer examination of the rate–pressure curve, however, has revealed that it sometimes has a segmented appearance, as though it were composed of several elementary curves, each characterised by a specific set of constants. Acetone, acetaldehyde, and propaldehyde, and also nitrous oxide, are examples of substances which yield this type of curve. It has been concluded that in these cases there are several varieties of activated molecule, differing in the location of the energy and having different decomposition probabilities (Hinshelwood, Fletcher, Verhoek, and Winkler, *Proc. Roy. Soc.*, 1934, *A*, **146**, 327).

The various activated states of the acetaldehyde molecule all lead to the same products, but with propaldehyde the nature of the decomposition products varies somewhat with pressure. In these two reactions the activation energy increases as the pressure falls, and to account for the observed rates more degrees of freedom must be invoked at low than at high pressures The rate–pressure curves for those modes of activation manifested in the lowest segments rise steeply but soon bend over. For these states the rate of activation is high, owing to the relatively large number of degrees of freedom which can contribute to the activation energy, while the decomposition probability is small on account of the correspondingly scattered distribution.

The most obvious interpretation of Fig. 3 is that nitric oxide considerably reduces the limiting height of that component which produces the first and steepest segment, leaving the other components unaffected.*

The first and steepest segment in the curve for propaldehyde is much longer than with acetaldehyde, as is evident from Fig. 4. In other words, the mode of activation manifested in this segment plays a considerably more important part in the decomposition of propaldehyde than in that of acetaldehyde.

The different types of activated acetaldehyde molecule all react as though the aldehydic hydrogen atom migrates to the alkyl carbon atom, with simultaneous rupture of the carbon–carbon link, giving carbon monoxide and methane. Similarly, the types of activated propaldehyde molecules responsible for the upper segments of the curve lead to carbon monoxide and ethane, but that type to which the first and steepest segment is due

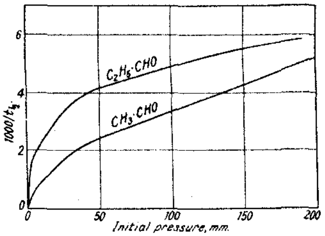
* The simplest way of analysing the curves is as follows. Rate, y, is plotted against pressure, x and tangents are drawn at many points; dy/dx is plotted against x, and a smooth curve drawn. Tangents are again drawn at many points, and d^2y/dx^2 plotted against x. More than one maximum of this curve indicates that the original curve could not have been described in terms of a single function because one type of decomposition probability would have to show a steady increase or decrease When this test is applied, multiple maxima cannot be avoided without obvious disregard of the experimental points.

undergoes an alternative decomposition, giving methane, ethylene, and hydrogen as primary products. This mode of activation, which is not possible for acetaldehyde, corresponds precisely to that segment of the rate–pressure curve, which with propaldehyde is suppressed by the nitric oxide.

Before the effect of nitric oxide was discovered, it had been suggested that in the reactions giving rise in each case to the lowest segment, the activation energy is located in the region of the molecule remote from the aldehyde groups, *i.e.*, in the C–H bonds of the alkyl groups, and that the greater prominence of this segment with propaldehyde is due to the larger alkyl group. In the case of acetaldehyde, the energy in the methyl group seems to be able to migrate ultimately into the vital part and cause dissociation into carbon monoxide and methane. But when the activation energy is distributed in the ethyl group in propaldehyde, production of a free radical becomes more likely. Thus it is conceivable that these activated propaldehyde molecules dissociate in some such manner as this: $CH_3{\cdot}CH_2{\cdot}CHO \longrightarrow CH_3 + CH_2{\cdot}CHO$, the methyl radicals then bringing about further decomposition, though it does not seem possible to advance any one mechanism for this chain process with certainty from the mere fact that it somehow leads to the ultimate formation of hydrogen, ethylene, methane, and carbon monoxide.

The question whether all active molecules or only some of them give chains has now been partially answered, since we have concluded that only those molecules in which the activation energy is large, and located in the region of the molecule most remote from the aldehyde group dissociate into radicals and so initiate chains or cause catalytic decomposition. But it is still uncertain whether all active molecules of this particular type yield chains, or only a fraction of them.

Fig. 4.



Comparison of acetaldehyde and propaldehyde: rate–pressure curves.

The activation energy of the uninhibited reaction increases as the pressure decreases, and our conclusion that it is the type of activated molecules with the largest activation energy which yields free radicals agrees with the observation of Patat and Sachsse (*Z. physikal. Chem.*, 1935, *B*, **31**, 105) that the concentration of free radicals set up during reactions is greater the nearer the observed activation energy is to the energy required to break the carbon–carbon link. It is significant in this connexion that the observed activation energy of the decomposition of acetaldehyde is about 9,000 cals. less than that for propaldehyde at the same initial pressure.

To account for the observed rate of the inhibited decomposition of propaldehyde at a pressure of 350 mm., the activation energy (51,000 cals.) must be assumed to be distributed in about 6 square terms, and at 30 mm. (when it is 58,500 cals.) in about 10.

Bearing of the Results on Current Theories of Unimolecular Reactions.—The two principal problems of unimolecular reactions are (*a*) to account for the high activation rate and (*b*) to account for the form of the curve connecting rate and pressure. Problem (*a*) is solved either by assuming the activation energy to be distributed in many degrees of freedom or by assuming long chains. In all examples to which the nitric oxide method has been applied, the average length of the chains is far too small for the second alternative. Moreover, even when all the chains are suppressed, many square terms are needed to account for the rate of the residual reaction. The activation energies require correction for variation of the chain length with temperature, and this alters the exact number of square terms required. In communications from this laboratory nothing has ever been concluded about the number of degrees of freedom involved, except that it is in general considerable though never unreasonably great, nor have correlations been suggested between this number and the structure of the molecules. This position is unchanged by the increase in the number required for the ethers and the decrease for propaldehyde. It remains to be seen whether

there are any correlations between structure and number of square terms for a series of chain-free reactions.

With regard to (*b*), in a chain-free reaction the form of the curve depends upon what function the transformation probability of activated molecules is of the magnitude and location of their activation energy. One view is that the probability varies continuously with the energy (Rice, Ramsperger, Kassel) and this is almost certainly correct in principle. But we believe the matter to be often more complex than this, in that the decomposition probabilities fall into groups, and give rise to what we have called the segmented curve. By this, we mean a curve requiring more than one function for its representation, and do not imply that it exhibits any discontinuity. Variable chain length might distort the curve and necessitate modification of either of these views. With ethyl ether, the form of the curve is unchanged by the suppression of the chains, which must therefore be of constant length, so that any conclusions about the transformation probabilities would be unaffected.

Apart from the fact that segmented curves are found with acetone, nitrous oxide, and acetaldehyde, where there are no chains, their existence is rendered more probable by the results with propaldehyde, which are best explained by supposing that nitric oxide affects one component only of a composite curve, the curve for the chain-free reaction still appearing to be composite.

SUMMARY.

The use of nitric oxide in small amounts as a chain detector has shown that the thermal decomposition of propaldehyde involves chains with an average length of about two units, but that that of acetaldehyde is free from chains. Both reactions are kinetically composite, and in the case of propaldehyde the nitric oxide suppresses a component not present with acetaldehyde. Chains appear to result only from a certain type of activated propaldehyde molecule, possibly one activated in the ethyl group, which has no counterpart in the reaction of acetaldehyde.

Correction of the activation energy for variation of chain length with temperature changes the number of square terms in which the activation energy must be assumed to be distributed, but makes no difference to existing views about the mechanism of activation.

We are indebted to Imperial Chemical Industries Ltd., for financial assistance.

PHYSICAL CHEMISTRY LABORATORY, BALLIOL COLLEGE AND TRINITY COLLEGE, OXFORD. [*Received, April 27th*, 1936.]

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189. *The Influence of Hydrogen on Unimolecular Reactions involving Short Chains.*

By C. N. HINSHELWOOD and L. A. K. STAVELEY.

HYDROGEN exerts a specific influence in preventing the falling off at low pressures of the velocity constants of unimolecular reactions (*Proc. Roy. Soc.*, 1927, *A*, **114**, 84; **115**, 215; **116**, 163). Three of the reactions thus affected have recently proved to involve short chains, namely, the decompositions of ethyl ether (Staveley and Hinshelwood, *Proc. Roy. Soc.*, 1936, *A*, **154**, 335), propaldehyde (*idd.*, *Nature*, 1936, **137**, 29), and methyl ether (unpublished work). The reaction mechanism does not depend upon long chains as in the schemes devised by Rice and Herzfeld for the decomposition of organic compounds (*J. Amer. Chem. Soc.*, 1934, **56**, 284), but corresponds much more closely to the state of affairs shown by the work of Patat and Sachsse (*Z. physikal. Chem.*, 1935, *B*, **31**, 105), where a few exceptional molecules give chains, the average length being short. This length can be determined by the addition of small amounts of nitric oxide, which cuts off the chains, and reduces the reaction velocity to a well-defined limit, representing the rate of the primary process or processes. That the reactions taking place in the presence of the nitric oxide may be regarded as free from chains has been confirmed in this laboratory (see preceding paper, p. 812).

Experiments have been made to find out what the influence of hydrogen on the chain-free reactions will be. It proves to be the same as for the completely uninhibited reactions, at least with ethyl ether and propaldehyde. This shows that the hydrogen influences the primary process and not the propagation of such chains as may be present.

The measurements have been made exactly as described in the various papers dealing with the separate reactions. Pure hydrogen, carefully freed from oxygen by passage over a red-hot filament, was used.

Table I shows that the ratio of the low-pressure rate with and without hydrogen is almost independent of the presence of the nitric oxide, although the inhibition caused by the latter is considerable, being 2- or 3-fold.

Table II contains the results for ethyl ether, and Figs. 1 and 2, taken in comparison with those in the earlier publications, show that the characteristic phenomena appear unchanged by the suppression of the chains. The important facts are (1) that with increasing additions of hydrogen the rate approaches a limit which is the same as that reached at high partial pressures of the ether itself, (2) that hydrogen restores the fallen low-pressure rate, but does not influence the high-pressure rate. The simple interpretation of this is that the hydrogen maintains the Maxwell–Boltzmann distribution among the activated molecules, but exerts no other important influence. (To the arguments given in previous papers, that hydrogen does not act by reducing the ether, may be added the following: the only likely reduction products are ethane and ethyl alcohol, of which the latter is very much more stable than ether itself, so that if formed it would remain and be detected. This does not happen.)

The form of the curves in Fig. 1 calls for a further comment. Steacie and Solomon (*J. Chem. Physics*, 1934, 2, 503) found the unimolecular constant for the ethyl ether decomposition to increase up to 200 atms. Thus, the curve for ether without hydrogen in Fig. 1 must retain a small negative slope even above several hundred mm., where it looks as though it would become horizontal. This is another example of the composite nature of many unimolecular reactions, in which the superposition of different activation mechanisms gives rise to a curve without discontinuities but of a definitely segmented form. The present results apply to the mode of unimolecular reaction predominating up to 1 atm. The common limits reached with high hydrogen and with high ether pressures are, of course, relative to the scale of pressures used. Several hundred atmospheres of ether will cause a different mechanism to predominate, and raise the rate beyond the limit we are dealing with now. So probably would the addition of several hundred atmospheres of hydrogen.

TABLE I.

Propaldehyde at 549°. Initial pressure 75 mm.

Press. of H_2, mm.	0	97	137	180	235	268	288	388	459	465	522
Ratio of rates of reaction with and without hydrogen — Without NO ...	1·00	1·10	—	1·26	—	1·38	—	1·48	—	1·47	—
Ratio of rates of reaction with and without hydrogen — With 2 mm. NO	1·00	—	1·18	—	1·29	—	1·37	1·50	1·49	—	1·59

TABLE II.

Ethyl ether and 5 mm. NO *at* 580°.

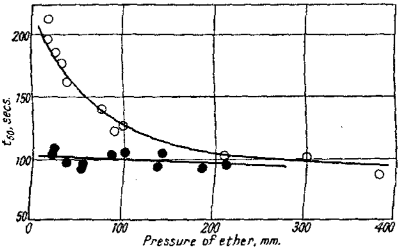
Ether, mm.	Hydrogen, mm.	t_{50}, sec.	Ether, mm.	Hydrogen, mm.	t_{50}, sec.	Ether, mm.	Hydrogen, mm.	t_{50}, sec.
378	0	87	211	403	96	35	0	180
300	0	102	186	392	93	42	86	147
210	0	103	136	396	95	35	174	130
142	0	105	100	388	107	35	214	111
99	0	128	88	394	105	37	359	102
90	0	123	56	421	97	33	546	93
77	0	142	54	432	94	(35	400	102)
42	0	163	23	409	110			
35	0	179	20·5	401	105			
29	0	186						
19·5	0	198						
19·5	0	215						

In Table II, t_{50} is the time required for the pressure to increase by 50% of the initial

value. Correction of the results for change of end-point with pressure slightly exaggerates the curvature of the upper curve in Fig. 1 at low pressures, but does not change the general shape or affect the convergence of the two curves. The use of t_{50} instead of initial rates has been criticised. If, however, initial rates are plotted instead of t_{50}, essentially similar relationships are found. At the low pressures, initial rates cannot be measured as accurately as t_{50} values. The latter have accordingly been preferred.

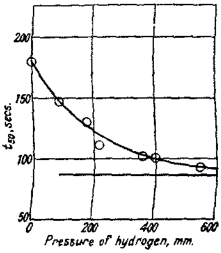
With methyl ether the average chain length proves to be longer (15—20 units), but nitric oxide is used up so quickly in chemical reactions that accurate measurements in presence of hydrogen are difficult. The behaviour of methyl ether with hydrogen is, however, so similar to that of ethyl ether that we may assume our conclusions about the latter

FIG. 1.



Decomposition of ethyl ether at 580°. Influence of hydrogen for different partial pressures of ether. Reaction inhibited by 5 mm. of nitric oxide. Open circles—no hydrogen present: shaded circles—ca. *400 mm. of hydrogen present. This figure should be compared with that for the uninhibited reaction* (*Fig. 1 of* Proc. Roy. Soc., 1927, *A*, **114**, 84).

FIG. 2.



Influence of various pressures of hydrogen on NO-*inhibited reaction of ethyl ether at* 580°. *Initial ether pressure* ca. 35 *mm. Horizontal line shows value for* 387 *mm. of ether without hydrogen.*

to apply also to the former. In their work with para-hydrogen, Patat and Sachsse point out that the presence of hydrogen would not be expected to affect the concentration of free radicals, since for each radical removed a hydrogen atom would be formed which at once attacks an organic molecule with regeneration of a free radical. The present results support this idea.

SUMMARY.

The influence of hydrogen on the unimolecular decompositions of propaldehyde and of ethyl ether has been investigated when all chains are suppressed by the addition of 2—5 mm of nitric oxide. The hydrogen can increase the rate of reaction to the value characteristic of high partial pressures of the reactant, but no further. The effect is quantitatively similar to that found for the uninhibited reactions, showing that the hydrogen acts by maintaining the energy distribution among the molecules concerned in the primary process and does not seriously influence such chains as may be present.

PHYSICAL CHEMISTRY LABORATORY, BALLIOL COLLEGE AND TRINITY COLLEGE, OXFORD. [*Received, April 27th*, 1936.]

190. *Studies in Electrolytic Oxidation. Part VII. The Electrolysis of Acetates in Non-aqueous Solutions.*

By S. GLASSTONE and A. HICKLING.

IN Part VI of this work (J., 1934, 1878) the electrolysis of acetates in aqueous solution was studied, and the conclusion drawn that the anodic evolution of ethane and carbon dioxide (Kolbe reaction) is due to the primary formation, by the irreversible combination of di

charged hydroxyl radicals, of hydrogen peroxide, which oxidises the acetate ions, probably with the intermediate production of acetate radicals and possibly acetyl peroxide. The conditions determining the supersession of the Kolbe synthesis by the Hofer–Moest reaction (formation of methyl alcohol) were determined, and it was concluded that this process is an oxidation by oxygen or by hydrogen peroxide of low concentration, and always takes place in aqueous solution when the Kolbe reaction is inhibited. The critical potential (2·14 volts) associated with the Kolbe reaction was regarded as being set up by discharged acetate radicals formed mainly indirectly. It now appeared of importance to investigate the electrolysis of non-aqueous solutions of acetates, since previous work had shown that the Kolbe synthesis can take place in such solutions; as hydroxyl ions are not present, however, the mechanism of the process must presumably be different from that proposed for an aqueous medium. Previous work, of a somewhat sporadic nature, had been carried out with acetic acid and methyl and ethyl alcohols as solvents (Hopfgartner, *Monatsh.*, 1911, **32**, 523; Salauze, *Bull Soc. chim.*, 1925, **37**, 522; *Compt. rend.*, 1925, **180**, 662; Fairweather and Walker, J., 1926, 3111; Shukla and Walker, *Trans. Faraday Soc.*, 1932, **28**, 457; Fichter and Meyer, *Helv. Chim. Acta*, 1933, **16**, 1408; Robertson, *Trans. Faraday Soc.*, 1934, **10**, 1007), but no comprehensive investigation had been made, although the results at elevated temperatures and with various anode materials were sufficient to show that the mechanism of the Kolbe synthesis was fundamentally different from that in aqueous solutions. In the present work, for reasons indicated below, ethylene glycol was used as solvent, and a full study has been made of the influence of all variable factors on the electrolytic process.

EXPERIMENTAL.

In searching for a suitable non-aqueous solvent, the appropriate properties of a number of organic liquids were studied. Acetic acid was rejected since it was not possible effectively to vary the acetate concentration in such a solution, or to work with solutions containing alkali hydroxides, and oxide-coated anodes could not be employed. Methyl and ethyl alcohols were judged unsuitable because of their limited solvent powers, and the difficulty of obtaining them completely anhydrous. Empirical investigation of a large number of organic liquids revealed that ethylene glycol was most suitable: it dissolves most electrolytes giving excellently conducting solutions, and owing to its high b. p. is readily obtained water-free by distillation alone. The glycol employed was purified by fractional distillation, the fraction, b. p. 197—198° (corr.), being used. Acetic acid was purified by the method of Orton and Bradfield (J., 1927, 983); m. p. 16·4°. The potassium acetate used was the commercial "pure" variety; it was powdered, heated in an air-oven at 110—115° for 4 hours, and kept in a vacuum desiccator over calcium chloride. For most of the experiments a stock solution of potassium acetate in the glycol was used; this was boiled for a few minutes previous to use to eliminate traces of water and dissolved gases, and it was then cooled and the requisite amount of acetic acid added.

The electrolytic vessel consisted of a water-jacketed boiling tube (6" × 1") fitted with a rubber stopper carrying a thermometer, electrodes, and capillary delivery tube leading to a small mercury trough. The cathode was a piece of stout platinum foil 1 cm. square; the anode was, in general, a spiral of platinum wire of 1 sq. cm. area. Anode and cathode were about 2 cm. apart, and the compartments were not separated unless otherwise stated. Before use, the anode was washed with warm concentrated hydrochloric acid, warm concentrated nitric acid, and water, and heated to redness. Current was supplied from a 40-volt battery through a rheostat and a calibrated milliammeter. 50 C.c. of electrolyte were used in each case. Preliminary electrolysis for 1 hour was found sufficient to saturate the electrolyte with ethane and to displace the air in the apparatus, and was carried out in all cases. In general, about 20-c.c. samples of the mixed anode and cathode gases were collected for analysis in a Bone–Newitt apparatus; carbon dioxide and oxygen were determined by absorption, and ethane and hydrogen by explosion. The sum of the analytical percentages is always close to 100, showing the amounts of other gases present to be negligible. Any methane is, of course, estimated as ethane and hydrogen (since $2CH_4 = C_2H_6 + H_2$), but the work of Shukla and Walker (*loc. cit.*) has shown that appreciable methane formation occurs only at *C.D.*'s lower than any employed in the present investigation. From the ethane/hydrogen ratio the current efficiency for ethane formation was obtained. (Check experiments, measuring the actual volume of ethane formed by the passage of a definite quantity of electricity, showed the method to be satisfactory.) Except where otherwise stated, all electrolyses were carried out at 20°.

Results.

(In the following experiments, a "stock solution" is one of *N*-potassium acetate and *N*-acetic acid in glycol.)

Influence of Duration of Electrolysis.—To determine the effect of duration of electrolysis and to investigate the reproducibility of the results, a stock solution was electrolysed at a *C.D.* of 0·05 amp./sq. cm., samples being collected after 1, 3, and 5 hours' electrolysis. In two sets of experiments the following results were obtained for the efficiency of ethane formation: (1) 69, 66, 65; (2) 66, 66, 63%. It is seen that, if other factors remain constant, duration of electrolysis itself has little influence on the efficiency. The results are in general reproducible to 2—3%.

Influence of C.D.—The influence of *C.D.* was investigated by electrolysing a stock solution with the usual current of 0·05 amp., the size of the anode being varied. The large anodes were of platinum foil and the small ones of platinum wire, all being treated previous to use in the same manner. The following results were obtained:

C.D., amp./sq. cm.	0·5	0·1	0·05	0·01	0·005
Efficiency, %	76	69	66	61	57

The efficiency evidently falls off somewhat with decreasing *C.D.*, although to a less extent than in aqueous solution (see Part VI); the relation between efficiency and *C.D.* is an approximately logarithmic one.

Influence of Concentration.—Experiments were made in solutions of varying total acetate concentration at a *C.D.* of 0·05 amp./sq. cm.; the results were as follows:

KOAc, *N*	1	0·5	0·25	0·1
HOAc, *N*	1	0·5	0·25	0·1
Efficiency, %	66	60	56	41

It may be noted that the efficiency falls off with decreasing concentration but not so markedly as in aqueous solution.

Variation of Proportions of Acid and Salt.—The effect of varying the proportions of potassium acetate and acetic acid while the total acetate concentration is kept constant is shown below, a *C.D.* of 0·05 amp./sq. cm. being used.

KOAc, *N*	0·25	0·5	0·75	1·0
HOAc, *N*	0·75	0·5	0·25	0
Efficiency, %	67	60	56	41

In glycol solution the efficiency falls off somewhat with decreasing acid concentration, although in aqueous solution a maximum efficiency was obtained with an electrolyte consisting of equimolar parts of salt and acid.

Influence of Temperature.—The following results were obtained at a number of temperatures with a stock solution and a *C.D.* of 0·05 amp./sq. cm.

Temperature	20°	40°	60°	80°	98°
Efficiency, %	66	70	69	60	53

It is observed that the efficiency at first rises and then falls with increasing temperature, there being a maximum at about 50°. In aqueous solution the efficiency falls continuously as the temperature is raised, and approximates to zero at 100°.

Influence of Anode Material.—In order to determine the influence of anode material a stock solution was electrolysed with a *C.D.* of 0·05 amp./sq. cm. with various anodes, the apparent area of each anode being 1 sq. cm. Prior to use, the platinised platinum anode was washed with concentrated hydrochloric acid, concentrated nitric acid, water, and acetone, and dried in a current of hot air. The gold anode was washed with concentrated hydrochloric acid, water, acetone, and dried as above. The carbon anodes were washed with water, and then dried after treatment with acetone as above. A nickel anode was tried, but it dissolved in the electrolyte with very little gas evolution. The results are given below.

Anode material	Pt.	Platinised Pt.	Au.	Arc C.	Graphite.
Efficiency, %	66	39	67	71	53

It appears that, if allowance is made for the fact that the actual *C.D.* at platinised platinum and graphite anodes (the latter disintegrated somewhat during electrolysis) is less than at the other anodes, anode material has very little influence on the efficiency, in contrast to its predominating effect in aqueous solution.

Influence of Addition of Water.—Since a gold anode in aqueous solution gives practically no ethane, it was thought of interest to ascertain the effect of small additions of water on the electrolysis in glycol solution. A stock solution was used with a *C.D.* of 0·05 amp./sq. cm. The following results were obtained.

Water, %	0	1	2	3	4	5	10
Efficiency, %	67	56	39	23	10	2	4

It will be noted that the efficiency falls off linearly with the addition of water, reaching the value for aqueous solution at a concentration of water of about 4·7%. To see if the effect of water changes with *C.D.*, experiments were carried out with the usual current of 0·05 amp., but with anodes of different sizes; the results are given below.

C.D., amp./sq. cm.	0·20	0·10	0·05
Efficiency with no water present, %	72	71	67
Efficiency with 4% water present, %	10	13	10

It is seen that within the limits of experimental error a given quantity of water has the same effect in reducing the efficiency independently of *C.D.* It is noteworthy that the addition of water to the glycol solution when a platinum anode is used actually raises the efficiency; *e.g.*, with a solution of *N*-potassium acetate and *N*-acetic acid in glycol and a current of 0·05 amp., the addition of 10% of water raised the efficiency from 66 to 73%.

Influence of Hydroxyl Ions.—To determine whether the water or the hydroxyl ions to which it gives rise are responsible for the inhibition of the synthesis at a gold anode, the effect was studied of adding an alkali hydroxide to the glycol solution. It is impossible to obtain any high concentration of hydroxyl ions, since the carbon dioxide formed at the anode will immediately use up any hydroxide in the vicinity, but it was thought that a small effect might be observed. A solution of *N*-potassium acetate and 0·02*N*-potassium hydroxide in glycol was electrolysed at a *C.D.* of 0·05 amp./sq. cm. with a smooth platinum anode and with a gold anode respectively. The results obtained were :

Anode material	Pt.	Au.
Efficiency, %	40	33

The very small concentration of hydroxyl ions has evidently about the same relative effect on the efficiency of synthesis at a gold anode as has 1% of water. It is probable, therefore, that hydroxyl ions are the effective agents in inhibiting the synthesis when water is added.

Influence of Catalysts for Hydrogen Peroxide Decomposition.—In aqueous solution the addition of small quantities of metallic salts which are catalysts for hydrogen peroxide decomposition inhibits the Kolhe synthesis. It seemed of interest, consequently, to ascertain their effects on electrolysis in the glycol solution. Complications due to the reduction of the metallic salt or deposition of metal at the cathode were avoided by the use of special electrolytic vessels in which the cathode and anode solutions could be separated. These vessels, made by Schott und Gen., of Jena, consisted of flat-bottomed test-tubes (6″ × 1″) divided longitudinally by a porous partition made of fritted glass (porosity G 4) extending to within an inch of the top of the tube. Anode and cathode, mounted in the usual way, were fitted on each side of the diaphragm. These cells were advantageous in that they could be cleaned and dried easily, had very low electrical resistance, diffusion of anolyte and catholyte was negligible, and anode and cathode gases could be collected together in the ordinary way. In all the experiments the catholyte used was 15 c.c. of the stock solution, and the anolyte was 15 c.c. of a solution of potassium acetate and *N*-acetic acid in glycol to which the metallic salt had been added. The catalysts were added as acetates, the solution being made 0·05*M* with respect to the added salt, and the total acetate concentration was *N*. Crystalline lead, manganese, cobalt and copper acetates were dehydrated by heating at 110° for 8 hours, and then kept in a vacuum over concentrated sulphuric acid for several weeks. Ferrous acetate was made directly by dissolving finely divided iron in anhydrous acetic acid. Electrolysis was carried out with the smooth platinum anode at a *C.D.* of 0·05 amp./sq. cm. The preliminary electrolysis was extended to 3 hours to permit complete oxidation of the metallic ions before gas was collected. The following efficiencies were observed :

Catalyst	(None).	Mn.	Pb.	Co.	Cu.	Fe.
Efficiency, %	66	63	66	69	59	64

It is clear that within the limits of experimental error the added substances have no appreciable action in reducing the efficiency, in contrast to their very marked effect in aqueous solution. On the addition of a small amount of water to the glycol solutions, the Kolbe synthesis was largely inhibited; thus the addition of 5% of water to the solutions containing manganese and

copper reduced the efficiencies to 13 and 4% respectively. In view of the observations of Walker and Weiss (*Trans. Faraday Soc.*, 1935, **31**, 1011), it is noteworthy that in neither case was there any visible deposition of oxide on the anode.

Oxide-coated Anodes.—It was thought desirable to ascertain if platinum anodes coated with metallic oxides which are catalysts for hydrogen peroxide decomposition would give the usual ethane efficiency in glycol solution, but difficulty was experienced in obtaining adherent oxide coatings. To help in this connexion, the oxides were deposited on grey platinum, the roughened surfaces serving to retain them, and *N*-potassium acetate in glycol was used as electrolyte; the oxides are less soluble than in the acid solution and the anodic gas evolution is less vigorous since much of the carbon dioxide is retained by the electrolyte. Lead dioxide was deposited by electrolysis of *N*-lead acetate in water at 0·50 amp. for 2 mins. Manganese dioxide was deposited by electrolysis of *N*-manganous acetate in water at 0·05 amp. for 5 mins. An oxide of cobalt could not be deposited. The oxide-coated electrodes were washed thoroughly with water, then with acetone, and dried in an air-oven at 115—120° for 2 hours. The electrolysis was then carried out with an undivided cell and a *C.D.* of 0·05 amp./sq. cm.; the results are given below:

Anode material	Pt.	PbO_2.	MnO_2.
Efficiency, %	41	2	41

It is seen that the manganese dioxide anode gives about the same efficiency as platinum, but the lead dioxide anode gives very little ethane. Observation of the rate of gas evolution at the beginning of the electrolysis seemed to indicate that the lead dioxide anode initially gave a good Kolbe synthesis, but after a time the coating became lighter in colour and the rate of gas evolution decreased, and by the time the preliminary electrolysis was completed very little ethane was being formed. It seems probable that this is a specific action of the lead dioxide (see below).

Potential Measurements.—In order to make measurements of the potentials at which ethane is formed in the glycol solutions, use was made of the commutator-extrapolation method (Glasstone, J., 1923, **123**, 2926; 1927, 642). The anode was provided with the usual Luggin capillary, and this was connected to a calomel electrode with aqueous electrolyte by a bridge containing stock solution, the ends of the syphon being closed by filter-paper plugs. The following values for the anode potential using various electrode materials were obtained at a *C.D.* of 0·032 amp./sq. cm. with *N*-potassium acetate and *N*-acetic acid in glycol as electrolyte; they are expressed on the hydrogen scale in water and all include the same liquid-junction potential.

Anode material	Pt.	Platinised Pt.	Au.	Graphite.	MnO_2.	PbO_2.
Potential, volts	2·16	2·06	2·13	2·13	2·15	1·69

With the exception of the lead dioxide anode, the potentials are approximately the same; the effective *C.D.* at platinised platinum is probably much lower than at the other anodes.

Anodic Oxidation of Glycol.—In none of the electrolytic experiments did the ethane efficiency approach 100%. The gas evolved consisted of ethane with the corresponding amount of carbon dioxide required by the equation for the Kolbe reaction, small but definite amounts of oxygen, usually about 1%, and hydrogen from the cathode. Part of the current must therefore go to oxidise the glycol, and it was found that the electrolytes after each experiment gave a precipitate with 2 : 4-dinitrophenylhydrazine, showing the presence of aldehyde.

Two initial aldehydic oxidation products of glycol are possible, *viz.*, glycollaldehyde and glyoxal. Glycollaldehyde-2 : 4-dinitrophenylhydrazone forms yellow needles, m. p. 155—156° (Collatz and Neuberg, *Biochem. Z.*, 1932, **255**, 29); but we fouud the m. p. to be greatly affected by minute traces of impurity. An aqueous solution of glycollaldehyde was obtained by hydrolysis of bromoacetaldehyde (Fischer and Landsteiner, *Ber.*, 1892, **25**, 2553) and precipitated with a saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride; the product, after recrystallisation from chloroform–light petroleum, melted fairly sharply at about 137° and gave a correct analysis. Subsequent repeated recrystallisation from 50% methyl alcohol raised the m. p., however, until an ultimate constant value of 158° (corr.) was obtained.

Glyoxal-2 : 4-dinitrophenylhydrazone was obtained as an orange-coloured powder by precipitating an aqueous solution of glyoxal with a saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride. It was only sparingly soluble in most organic solvents and was best recrystallised from nitrobenzene. It then appeared as reddish-orange needles, m. p. 330° (corr.). Decomposition set in a few degrees above the m. p. (Found: C, 39·8; H, 2·4; N, 25·6.* $C_{14}H_{10}O_8N_8$ requires C, 40·2; H, 2·4; N, 26·8%).

* On heating, the substance formed a nitrogenous charcoal which is difficult to burn completely.

To obtain the anodic oxidation products of glycol in quantity, a solution of *N*-potassium acetate and *N*-acetic acid in glycol was electrolysed at 0·05 amp. with the smooth platinum anode under the usual conditions for 14 hours. The solution was then diluted, and a saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride added. A yellow precipitate was formed immediately, and after standing for 30 mins., was filtered off and dried; m. p. 140—150°. On recrystallisation from 50% methyl alcohol, it had m. p. 150—152° (corr.). A further recrystallisation gave yellow needles, m. p. 158° (corr.). The oxidation product would therefore appear to be glycollaldehyde. To gain some idea of its amount, a fresh electrolyte solution was electrolysed at 0·05 amp. for 3 hours. The liquid was then diluted, excess of an ice-cold saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride added, and the mixture kept over-night at 0°. The precipitate was then collected in a weighed glass crucible, washed with water, and dried to constant weight at 105—110°. In two experiments the weights of precipitate obtained were 0·102 and 0·106 g., corresponding to a mean value of 16% for the current efficiency of glycollaldehyde formation. As it is unlikely that the hydrazone is completely precipitated, the actual efficiency will probably be greater than this. The ethane efficiency in the electrolysis is 66%, and allowance being made for the small amount of oxygen evolved, it seems evident that glycollaldehyde formation will account for the greater part of the remainder of the current. The result, therefore, seems to leave no doubt that the main product of the anodic oxidation of glycol in the present experiments is glycollaldehyde.

Action of Acetyl Peroxide on Glycol.—For reasons indicated below, the action of acetyl peroxide on glycol was investigated. 1·3 G. of acetyl peroxide dissolved in 15 c.c. of dry ether were added to 20 c.c. of glycol and heated on a water-bath for 30 mins. On testing with potassium iodide, the peroxide was then found to have been completely used up. The liquid was cooled, diluted with water, and excess of an ice-cold saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride added. An immediate yellow precipitate resulted, which was collected and weighed as before, 2·414 g. being obtained, corresponding to a 91% yield of glycollaldehyde calculated on the weight of peroxide taken. The product melted at 152—155° (corr.), and a single recrystallisation from 50% methyl alcohol gave yellow needles, m. p. 158° (corr.).

Discussion.

Since solutions of acetates in glycol have a reasonably good conductivity, and decomposition occurs without the application of excessive voltages, it is evident that acetate ions are readily discharged at the anode, and that the resulting radicals are essentially responsible for the Kolbe reaction which occurs. Apart from this process, however, there are two outstanding observations on the electrolysis of acetate solutions in glycol requiring consideration : these are (*a*) the formation of considerable amounts of glycollaldehyde at any anode, and (*b*) the inhibition of the Kolbe synthesis at a lead dioxide anode. It is highly improbable that oxidation of glycol to glycollaldehyde is a purely electrical process, for, not only is the reaction difficult to formulate, but there is no reason to believe that an alcohol and an aldehyde constitute a definite oxidation–reduction system. It appears, therefore, that chemical oxidation occurs, and in the electrolysis of acetates the effective oxidising agent is probably either the discharged acetate radicals or acetyl peroxide, formed by the combination of these radicals in pairs. The fact that acetyl peroxide reacts readily with glycol, as already described, to give an almost quantitative yield of glycollaldehyde, suggests that the peroxide may well be the active oxidising agent.

This view is supported by the anomalous behaviour of the lead dioxide anode. It was found that on warming lead dioxide for a short time with glycol, oxidation took place and the oxide became yellow; on pouring off the excess glycol and adding a solution of acetyl peroxide in ether, the residue caused vigorous decomposition and evolution of oxygen. The same phenomenon was shown by lead monoxide when mixed with acetyl peroxide in ethereal solution, but the decomposition was only vigorous if a trace of glycol was present. Lead dioxide itself, manganese dioxide, and cobalt sesquioxide did not bring about any decomposition under similar conditions; silver oxide had a slight effect. In electrolysis with the lead dioxide anode, therefore, it would appear that the lead dioxide is slowly reduced by the glycol, and the lead monoxide formed then brings about decomposition of the acetyl peroxide and so inhibits the Kolbe synthesis; this corresponds closely with the experimental observations. The decomposition of acetyl peroxide by lead monoxide is

accompanied by oxygen evolution, but at an anode initially covered with lead dioxide the amount of oxygen in the electrolytic gas is no greater than at other electrodes. In view of the ease with which glycol can be oxidised by nascent oxygen, this result is not surprising. It may be noted, however, that the small amounts of oxygen which are always found in the electrolytic gases may possibly be due to decomposition of the acetyl peroxide.

Since it is necessary to postulate the formation of this peroxide to account for the two observations mentioned above, it is reasonable to assume that all the discharged acetate radicals combine in pairs to give acetyl peroxide. At most anodes, part of it then decomposes to give ethane and carbon dioxide (cf. Walker, *J.*, 1928, 2040; Walker and Wild, *J.*, 1935, 207), and the remainder is utilised in oxidising the glycol. Since acetyl peroxide is hardly affected by any of the anode materials used, apart from lead dioxide after reduction to the monoxide, the Kolbe synthesis in glycol is largely independent of the nature of the anode and of the presence of catalysts for hydrogen peroxide decomposition. On heating, acetyl peroxide tends to decompose into hydrocarbons and carbon dioxide, and hence the electrosynthesis is not greatly affected by rise of temperature, except in so far as the rate of oxidation of the glycol is probably increased. Similarly, other electrolytic factors such as *C.D.* and concentration have only slight effects in non-aqueous solution.

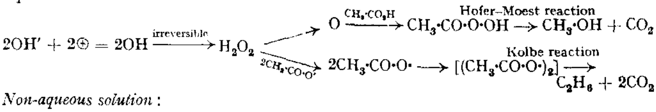
The view that peroxides are intermediates in electrosynthetic reactions with the salts of fatty acids and with the acid-ester salts of dibasic acids has been advocated by Fichter and his collaborators (see Glasstone and Hickling, "Electrolytic Oxidation and Reduction," 1935, pp. 293—295; Fichter *et al., Helv. Chim. Acta*, 1935, **18**, 18, 238, 445, 549, 704, 1005, 1276; 1936, **19**, 149; see also Wieland, Schapiro, and Metzger, *Annalen*, 1934, **513**, 93), mainly as a result of the observed similarity between the electrolytic products and the substances obtained by decomposition of, or chemical interaction with, the appropriate peroxide. In a few instances small amounts of peroxides have actually been detected at the anode by electrolysis under suitable conditions. Fichter, however, has generally held the opinion that the peroxides are not formed from discharged anions, but as a result of chemical oxidation by nascent oxygen. In view of the facts that such oxidation is very improbable in glycol solution, and that the potential at which the Kolbe reaction occurs in this medium is almost constant for a number of different anode materials (p. 822), it is more reasonable to suppose that acetyl peroxide, at least when glycol is the solvent, is formed by the union of discharged acetate radicals. Further, the agreement between the anode potentials in glycol, the liquid-junction being assumed to be small, with that (2·14 volt) required for the Kolbe reaction at a platinum anode in aqueous solution (Shukla and Walker, *Trans. Faraday Soc.*, 1931, **27**, 722; see also Part VI, *loc. cit.*), suggests that if peroxide is formed in the latter solution, as the work of Fichter implies, then it probably arises in this instance also from discharged acetate radicals. The influence of catalysts for hydrogen peroxide decomposition and of neutral salts makes it necessary to suggest, however, that in aqueous solution the radicals are formed mainly as a result of reaction of the acetate ions with hydrogen peroxide, and only to a slight extent by direct discharge at the anode.

On the addition of water or hydroxyl ions to the glycol solutions, hydroxyl-ion discharge will replace that of acetate ions, and if conditions are such as to favour the decomposition of the hydrogen peroxide formed, the Kolbe synthesis will be inhibited. This is seen to be the case in the experiments with the gold anode and in the presence of metallic salts. With small quantities of water the extent to which the synthesis is inhibited will depend upon the amount of water added. When the water present is able to reach the anode at a sufficient rate to provide hydroxyl ions to cope with the whole of the current passing, then direct acetate-ion discharge will no longer occur. As the limiting rate of diffusion of water to the anode under the existing concentration gradient will be very small in the viscous glycol solutions, it is probable that the water is carried to the anode by hydrated acetate ions. This would account for the fact that the influence of a given amount of water is independent of *C.D.*

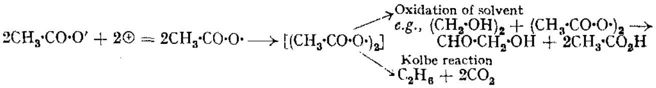
The conclusions reached concerning the electrolysis of acetates in glycol solution would seem to apply equally well to the observations reported with other non-aqueous solutions. Where the solvent is such as not to be readily oxidised, *e.g.*, acetic acid, then the acetyl

approximates to 100%. In conjunction with the results of the work in aqueous solution (Part VI) it is possible to present the following comprehensive scheme for the mechanism of the anodic oxidation of acetates.

Aqueous solution:



Non-aqueous solution:



It must be pointed out that if the first stage of the decomposition of acetyl peroxide in all reactions is the formation of acetate radicals, then the electrolytic results can be explained without the necessity of postulating the intermediate formation of the peroxide, the radicals being the effective agents in both the electrochemical and the chemical processes. At present, it appears impossible to decide between the two interpretations, for even the anodic production of acetyl, or other, peroxide in appreciable amounts would not necessarily be decisive.

SUMMARY.

1. A comprehensive investigation has been made of the electrolysis of acetates in glycol solution with special reference to the Kolbe synthesis: the influence of duration of electrolysis, of *C.D.*, of total acetate concentration, of the ratio of potassium acetate to acetic acid, of temperature, of anode materials (smooth and platinised platinum, gold, arc-carbon, graphite, and manganese and lead dioxides), of small amounts of water, of hydroxyl ions, and of catalysts for the decomposition of hydrogen peroxide, has been studied.

2. The current efficiency for the formation of ethane is generally of the order of 60%, except with a lead dioxide anode, the remainder of the current being mainly devoted to oxidation of the glycol to glycollaldehyde. At an anode initially coated with lead dioxide, which is reduced to the monoxide, the Kolbe efficiency is very low.

3. The anode potentials at which the Kolbe reaction occurs were measured at smooth and platinised platinum, gold, graphite, manganese and lead dioxide anodes: with the exception of the last, the values were almost constant.

4. Acetyl peroxide readily oxidises glycol quantitatively to glycollaldehyde, and the peroxide is rapidly decomposed by lead monoxide, yielding oxygen, especially in the presence of a small amount of glycol. Other oxides, *e.g.*, lead and manganese dioxides, cobalt sesquioxide, and silver oxide, and metals, *e.g.*, platinum and gold, have little action.

5. The results are explained by assuming that acetate ions are discharged at the anode and the resulting radicals combine in pairs to form acetyl peroxide: the latter either decomposes to give ethane and carbon dioxide (Kolbe reaction), or it oxidises the solvent, or it may be decomposed to give oxygen, *e.g.*, by lead monoxide. A scheme for the mechanism of the electrolysis of acetates in aqueous and non-aqueous solutions has been drawn up. It is pointed out that there appears to be no definite means of deciding whether the acetate radical or acetyl peroxide is the effective anodic intermediate.

6. Glyoxal-2 : 4-dinitrophenylhydrazone has been prepared and characterised.

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191. *A Synthesis of* cis- *and* trans-dl-1-iso*Propyl*cyclo*propane-1 : 2-dicarboxylic Acids.*

By E. O. Phillips, G. R. Ramage, and J. L. Simonsen.

Umbellularic acid (Tutin, J., 1906, **89**, 1104) was shown by Semmler (*Ber.*, 1907, **40**, 5017; 1908, **41**, 3988) to be *d-cis*-1-*iso*propyl*cyclo*propane-1 : 2-dicarboxylic acid (II). Our attention was directed to this acid by its resemblance to norcaryophyllenic acid (compare Evans, Ramage, and Simonsen, J., 1934, 1808) and it appeared of interest to undertake its synthesis.* By adaptation of the method used by Owen and Simonsen (J., 1933, 1225) for the synthesis of homocaronic acid, *ethyl* 1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylate* was readily prepared by the condensation of ethyl α-*iso*propylacrylate (I) (Blaise and Luttringer, *Bull. Soc. chim.*, 1905, **33**, 777) with ethyl diazoacetate. Hydro-

$$\text{(I.)}\quad CH_2{:}CPr^{\beta}{\cdot}CO_2Et \xrightarrow{N_2CH_2{\cdot}CO_2Et} EtO_2C{\cdot}CH{-}CPr^{\beta}{\cdot}CO_2Et\ (\text{with } CH_2 \text{ bridging}) \quad \text{(II.)}$$

lysis of the ester gave a mixture of the *cis*- and the *trans-dl*-form of the cyclic acid, in which the latter predominated. The trans-*acid*, m. p. 194—195°, was anhydrous, but the cis-*acid*, m. p. 97—98°, like umbellularic acid, crystallised from water with one molecule of water of crystallisation, which was lost at 100°, giving the anhydrous acid, m. p. 126—127°.

The structure assigned by Blaise and Luttringer to the acrylic ester has been confirmed by its oxidation with ozone to ethyl dimethylpyruvate. It is apparently free from isomerides.

It is proposed to extend this method of synthesis to the higher homologues of 1-*iso*-propyl*cyclo*propane-1 : 2-dicarboxylic acid.

Experimental.

Oxidation of Ethyl α-iso*Propylacrylate.*—The ester (3 g.) in carbon tetrachloride (25 c.c.) was ozonised, formaldehyde being identified in the issuing gas by the preparation of the dimedone derivative, m. p. and mixed m. p. 186°. The ozonides from three such oxidations were decomposed by water, no acetone being detected; the oil was collected in ether; after being washed with sodium carbonate solution and dried, the extract gave ethyl dimethylpyruvate (4 g.), b. p. 165—178°/769 mm. (semicarbazone, m. p. 92°). This ester was hydrolysed with methyl-alcoholic potassium hydroxide solution to dimethylpyruvic acid, b. p. 70—80°/20 mm., which was characterised by its 2 : 4-dinitrophenylhydrazone, m. p. 194—195° (compare Ramage and Simonsen, J., 1935, 535) (Found: C, 44·5; H, 4·3. Calc.: C, 44·6; H, 4·1%).

Condensation of Ethyl α-iso*Propylacrylate and Ethyl Diazoacetate.*—Ethyl diazoacetate (16 g.) was added slowly to ethyl α-*iso*propylacrylate (20 g.) at 75—80°. This temperature was maintained for 5 hours, and the mixture then heated on the water-bath until evolution of nitrogen ceased. The product from four such experiments was fractionated at 20 mm. and gave (i) b. p. 50—70° (20 g.), (ii) 120—150° (44 g.), and (iii) 190—210° (80 g.). Refractionation of (ii) gave *ethyl* 1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylate* (40 g.), b. p. 130—135°/20 mm. (Found: C, 62·7; H, 8·4. $C_{12}H_{20}O_4$ requires C, 63·2; H, 8·8%). Fraction (iii), which contained nitrogen, was heated at 150° with copper-bronze (20 g.) until evolution of nitrogen ceased; after fractionation a further quantity of the pure cyclic ester (51 g.) was obtained.

The ester (76 g.) was digested with a solution of potassium hydroxide (66 g.) in methyl alcohol (320 c.c.) for 1 hour on the water-bath, the alcohol removed, and the aqueous solution acidified. The gummy acid which separated was extracted with ether, and the solution dried and evaporated, leaving a partially crystalline residue, which was triturated with warm benzene. After filtration, the acid (31 g.; m. p. 188°, softening 160°) was recrystallised from hot water and gave dl-trans-1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylic acid* in prisms, m. p.

* When these experiments were nearing completion we learnt that Dr. H. N. Rydon also had synthesised the *cis*- and the *trans*-modification of the *cyclo*propane acid by a different method. We agreed to leave the resolution of the two acids into their optical antipodes in his hands and the results are described in the succeeding communication.

194—195°, unaltered by further crystallisation (Found : C, 55·8; H, 6·9; *M*, 172. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%; *M*, 172). The *trans*-acid is somewhat sparingly soluble in cold water, less so in benzene and chloroform, and readily soluble in acetone and ethyl acetate. It was stable to potassium permanganate in alkaline solution and it did not give a sparingly soluble copper salt with copper acetate solution. The p-*phenylphenacyl* ester crystallised from ethyl acetate or acetone in prismatic needles, m. p. 175—176° (Found : C, 76·9; H, 5·8. $C_{36}H_{32}O_6$ requires C, 77·1; H, 5·7%).

The solvent was removed from the benzene solution, from which the *trans*-acid had been separated, and the residue was digested for 1 hour with an excess of acetyl chloride. After removal of the excess of acid chloride, the oil was dissolved in ether and the ethereal solution was washed with ice-cold sodium bicarbonate solution, which removed some *trans*-acid (0·3 g.), dried, and evaporated. Distillation of the residue gave an oil (15 g.), b. p. 138—140°/20 mm., which on digestion with water furnished dl-cis-1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylic acid monohydrate* crystallising in stout prisms, m. p. 97—98°, unaltered by further crystallisation (Found : C, 50·4; H, 7·5; loss at 100°, 10·0; *M*, 189. $C_8H_{12}O_4,H_2O$ requires C, 50·5; H, 7·4; H_2O, 9·5%; *M*, 190). The hydrated acid was readily solnble in all the ordinary organic solvents except ligroin. The *anhydrous acid* crystallised slowly from benzene–ligroin in stellate clusters of needles, m. p. 117—118° (Found : C, 55·4; H, 7·3. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). This was apparently a labile form, since after four months the m. p. was 126—127°. The p-*phenylphenacyl* ester crystallised from acetic acid in rosettes of prismatic needles, m. p. 116—117° (Found : C, 76·9; H, 5·7. $C_{36}H_{32}O_6$ requires C, 77·1; H, 5·7%).

The *cis*-acid was prepared also by heating the *trans*-acid (3 g.) with acetic anhydride (9 g.) at 220° for 6 hours; fractionation of the product gave the *cis*-anhydride (2·3 g.), b. p. 138—140°/20 mm., from which the hydrated *cis*-acid (2·8 g.), m. p. 97—98°, was obtained on digestion with water.

We are indebted to the Government Grants Committee of the Royal Society, to the Chemical Society, and to Imperial Chemical Industries Limited for grants.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, March 24th,* 1936.]

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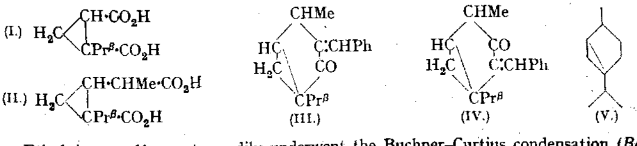
192. *The Synthesis of Umbellularic Acid; a Synthetic Proof of the Presence of the* cyclo*Propane Bridge in the Terpenes of the Thujane Series.*

By H. N. RYDON.

SEMMLER (*Ber.*, 1907, **40**, 5019; 1908, **41**, 3988) showed that umbellularic acid, obtained by Tutin (J., 1906, **89**, 1104) by the degradation of umbellulone, has the structure (I) and, further, established a connection between umbellulone and thnjone (and thus all the other members of the thujane series) by showing that enantiomorphous homothujadicarboxylic acids (II) were obtained by the oxidation of benzylidene-β-dihydroumbellulone (III) and of benzylidenethujone (IV). The present work provides synthetic proof of the presence of the *iso*propyl*cyclo*propane system in umbellulone and the terpenes of the thujane series, for which the carbon skeleton (V) (Semmler, *Ber.*, 1900, **33**, 275) has been accepted for many years, although no synthetic evidence for this has previously been put forward.



Ethyl *iso*propylfumarate readily underwent the Buchner–Curtius condensation (*Ber.*, 1885, **18**, 2371; 1890, **23**, 703; cf. v. Auwers and Ungemach, *Annalen*, 1934, **511**, 152) with diazomethane. The resulting pyrazoline lost nitrogen on distillation, yielding *ethyl*

1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylate.* Hydrolysis of this gave an easily separable mixture of the *dl-cis-* and *-trans*-acids.

dl-trans-1-iso*Propyl*cyclo*propane*-1 : 2-*dicarboxylic acid* (I) had m. p. 197°, and was readily resolved by means of its neutral *brucine* salt. The active acids melted at 155° and had $[\alpha]_{5461}$ +232·1° and − 236·2°; the crystalline form of the active acids was markedly different from that of the *dl*-acid and they were also considerably more soluble in water.

dl-cis-1-iso*Propyl*cyclo*propane*-1 : 2-*dicarboxylic acid* (I) crystallised from water as the *monohydrate,* m. p. 98—99°; the anhydrous acid crystallised from benzene–light petroleum had m. p. 126—127°. The resolution of this acid was considerably more troublesome than that of its stereoisomeride, but was eventually achieved by means of the acid brucine salt. The active *acids* crystallised from water as *monohydrates,* m. p. 78—79°, somewhat more soluble in water than the *dl-cis*-acid; these lost water at 100° or in a vacuum over phosphoric oxide and the resulting anhydrous acids, crystallised from benzene–light petroleum, had m. p. 119—120°, $[\alpha]_D$ + 86·9° and − 88·8°; Tutin (*loc. cit.*) found $[\alpha]_D$ − 89·7° for his acid.

Tutin (*loc. cit.*) records m. p. 85° for the monohydrate of umbellularic acid; his original specimen (for which I am indebted to Professor Simonsen), however, on examination melted at 78°, not depressed by synthetic *l-cis-1-iso*propyl*cyclo*propane-1 : 2-dicarboxylic acid monohydrate (confirmed by Professor Simonsen); on dehydration at 100° Tutin's specimen yielded the anhydrous acid, m. p. 119—120°, not depressed by the synthetic anhydrous *l-cis*-acid. It is thus evident that umbellularic acid has the structure (I) assigned to it by Semmler (*loc. cit.*).

Experiments are in progress to confirm the relationship between thujone and umbellulone by the degradation of thujadicarboxylic acid to umbellularic acid.

Experimental.

iso*Propylfumaric Acid.*—The following is a modification of Walden's method (*Ber.*, 1891, **24**, 2038; cf. Ssemenoff, *J. Russ. Phys. Chem. Soc.*, 1899, **30**, 1003). 110 G. of bromine were added dropwise during 40 minutes to 57 g. of ethyl *iso*propylacetoacetate in 100 c.c. of anhydrous ether. The hydrogen bromide and ether were then removed on the water-bath, and the cooled product added during 15 minutes with shaking to a mixture of 105 g. of powdered potassium hydroxide and 62 c.c. of absolute alcohol, the vigorous reaction being moderated by water-cooling (volatile products are formed which have an irritant action on the skin and eyes). The product was heated under reflux on the water-bath for 30 minutes and then steam-distilled, 300 c.c. of distillate being collected. The acidified residue deposited the crude acid, which was crystallised from water; yield, 22 g. (42%), m. p. 184—186°.

The ethyl ester was prepared by refluxing the acid (50 g.) for 24 hours with absolute alcohol (145 c.c.), benzene (225 c.c.), and sulphuric acid (33 c.c.). The product was poured into water, extracted with benzene, washed with sodium carbonate solution and water, dried, and distilled; yield, 47 g. (69%), b. p. 117—118°/21 mm., 91—92°/1·5 mm.

Condensation of Ethyl iso*Propylfumarate and Diazomethane.*—16 G. of the ester, dissolved in 50 c.c. of ether, were added to an ethereal solution (200 c.c.) of diazomethane prepared from 10 g. of methylurea (Arndt, " Organic Syntheses," 1935, **15**, 3). The mixture was kept (at first in ice) until the yellow colour had faded (14 days). The ether was removed in a vacuum, and the viscous residue distilled; vigorous decomposition set in at 160° (bath temperature) and the product (16 g.) distilled at 126—130°/18 mm. Redistillation afforded 14 g. (82%) of *ethyl* 1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylate* as a colourless liquid with a faint pleasant smell, b. p. 121—122°/13 mm., 94—96°/0·6 mm. (Found: C, 63·3; H, 8·8. $C_{12}H_{20}O_4$ requires C, 63·2; H, 8·8%). The ester was practically unchanged after refluxing for 24 hours with concentrated hydrochloric acid (3 vols.).

14 G. of the ester were refluxed on the water-bath for 3 hours with a solution of potassium hydroxide (14 g.) in ethyl alcohol (56 c.c.). The product was poured into water and, after removal of neutral products with ether, acidified and thoroughly extracted with ether. Evaporation of the ether left the crude acid (8 g.; 75%) as a semi-solid mass. This was triturated with 10 c.c. of acetyl chloride; the insoluble portion was filtered off and proved to be the crude *trans*-acid, m. p. 192—195°; crystallisation from water afforded dl-trans-1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylic acid* in magnificent flattened prisms, m. p. 197° [Found: C, 55·6; H, 6·9; equiv. (by titration), 86·0. $C_8H_{12}O_4$ (dibasic) requires C, 55·8; H, 7·0%; equiv.,

86·0]. The acetyl chloride filtrate was poured into water and evaporated several times on the water-bath, water being added when necessary. Crystallisation of the product from water yielded dl-cis-1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylic acid monohydrate* in massive prisms, m. p. 98—99° (Found : C, 50·6; H, 7·5; H_2O, 9·3. $C_8H_{12}O_4,H_2O$ requires C, 50·5; H, 7·4; H_2O, 9·5%). The water of crystallisation was lost in a vacuum over phosphoric oxide; the *anhydrous acid* obtained crystallised (in a phosphoric oxide desiccator) from benzene–light petroleum (both dried over phosphoric oxide *) in rosettes of fine needles, m. p. 126—127° (Found : C, 56·1; H, 6·9%).

In another experiment, the hydrolysis product from 38 g. of the ester was poured into 200 c.c. of water, and the alcohol evaporated on the water-bath. Acidification gave 14·3 g. (50%) of crude *trans*-acid, m. p. 191—193°, and extraction of the filtrate afforded 8 g. (28%) of crude *cis*-acid, which was crystallised from water.

The *cis*-acid was also prepared by heating the *trans*-acid (14·5 g.) with acetyl chloride (5 vols.) in a sealed tube for 6 hours at 220°; the product was poured into water. After several evaporations with water the *cis*-acid obtained was crystallised from water (charcoal); yield, 13·0 g., m. p. 98—99°.

Resolution of the trans-*Acid*.—8 G. of the acid were dissolved in 1700 c.c. of hot water, and 40 g. (2 mols.) of powdered brucine added in small portions, with stirring. After 12 hours, the neutral *brucine* salt of the *l*-acid (19·8 g.) was deposited in feathery aggregates of prisms, m. p. 149—151° (decomp.), $[\alpha]_{5461}^{25°}$ − 98·8° (l = 2, c = 2·060 in chloroform), unchanged on recrystallisation (Found : C, 60·9; H, 7·1. $C_{54}H_{64}O_{12}N_4,6H_2O$ requires C, 60·7; H, 7·1%). This salt was decomposed with ammonia, the brucine removed by filtration, and the residual solution acidified and extracted with ether. The dried extract, on evaporation, yielded 3·27 g. (41%) of crude *l*-acid; on crystallisation from water, this yielded interlacing clusters of fine needles consisting of l-trans-1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylic acid*, m. p. 155°, $[\alpha]_{5461}^{21°}$ − 236·2° (l = 2, c = 1·317 in acetone) (Found : C, 56·0; H, 6·9%).

On evaporation of the mother-liquor from the brucine salt of the *l*-acid, a crop of needles (13·7 g.) was obtained. On recrystallisation this afforded the neutral brucine salt of the *d*-acid in prismatic needles (12·3 g.), $[\alpha]_{5461}^{22°}$ − 15·39° (l = 2, c = 2·047 in chloroform), unchanged by further crystallisation. This was decomposed with ammonia in the usual manner; the recovered acid was crystallised from water, yielding d-trans-1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylic acid* in radiating clusters of fine needles, m. p. 155°, $[\alpha]_{5461}^{17°}$ + 232·1° (l = 2, c = 0·983 in acetone) (Found : C, 55·9; H, 7·15%). A mixture of this acid and the *l*-*trans*-acid melted at 194—195°.

Resolution of the cis-*Acid*.—6·6 G. of the monohydrate of the *dl*-*cis*-acid were dissolved in 200 c.c. of hot water, and 16·5 g. (1 mol.) of brucine stirred in. After 12 hours, a mixture (15·08 g.) of plates and needles was deposited. Six crystallisations from water afforded the pure acid brucine salt (5·61 g.) of the *d*-acid in transparent plates, m. p. 110—120° (decomp.), $[\alpha]_{5461}^{20°}$ + 6·2° (l = 2, c = 2·020 in acetone). On decomposition with ammonia in the usual manner, these yielded 1·49 g. of the *d*-*cis*-acid. d-cis-1-iso*Propyl*cyclo*propane*-1 : 2-*dicarboxylic acid monohydrate* crystallised from water in interlacing, stout, prismatic needles, m. p. 78—79° (Found : C, 50·4; H, 7·3; H_2O, 9·5%). The *anhydrous acid* crystallised from benzene–light petroleum (b. p. 60—80°) in rosettes of stout elongated prisms, m. p. 119—120°, $[\alpha]_D^{16°}$ + 86·9° (l = 2, c = 1·221 in chloroform) (Found : C, 55·6, 55·8; H, 7·2, 7·1%).

A long series of systematic fractional crystallisations of the mother-liquors failed to yield the *l*-acid in a state approaching purity. A similar lack of success attended conversion into the neutral brucine salt and attempts to use cinchonine, cinchonidine, and strychnine for the resolution. After many trials the pure *l*-acid was obtained by the following procedure. 13·0 G. of the monohydrate of the *dl*-*cis*-acid were dissolved in 500 c.c. of hot water, and 31·9 g. (1 mol.) of powdered recrystallised brucine (tetrahydrate) stirred in. The solution deposited over-night 32·6 g. of a mixture of plates and needles, the former much more rapidly than the latter. The mixture was accordingly crystallised from 600 c.c. of water and the resulting first crop of plates (brucine salt of the *d*-acid) was filtered off after 3 hours while the solution was still slightly warm. The filtrate was heated to boiling and kept over-night; the resulting crop of needles, after one recrystallisation, yielded the pure acid brucine salt of the *l*-acid (6·9 g.) in prismatic needles, $[\alpha]_{5461}^{16°}$ − 29·5° (l = 2, c = 1·982 in acetone), unchanged by further crystallisation. This was decomposed with ammonia in the usual manner; crystallisation of the product (2·0 g.) from water yielded l-cis-1-iso*propyl*cyclo*propane*-1 : 2-*dicarboxylic acid monohydrate* in interlacing,

* It is essential to observe these precautions, since the ordinary solvents contain sufficient water for the acid to crystallise as the monohydrate, m. p. 99°.

stout, prismatic needles, m. p. 78—79° (Found : C, 50·4; H, 7·4; H_2O, 9·8%). The ***anhydrous acid*** crystallised from benzene–light petroleum (b. p. 60—80°) in rosettes of prisms, m. p. 119—120°, $[\alpha]_D^{16°}$ – 88·8° (l = 2, c = 2·020 in chloroform) (Found : C, 56·2; H, 7·1%).

A mixture of approximately equal amounts of the anhydrous *d*- and *l*-*cis*-acids melted at 106°, and a similar mixture of the monohydrates at 99° after softening at 76°.

The author is indebted to Professor J. L. Simonsen, F.R.S., for his kind encouragement and for generous gifts of the inactive acid prepared by another method (preceding paper), to Dr. F. Barrow for providing facilities for micro-analysis, and to the Government Grants Committee of the Royal Society for a grant.

IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, March 24th*, 1936.]

193. *The Thermal Decomposition of Silver Oxalate. Part I. Experimental.*

By J. Y. MACDONALD.

THE thermal decomposition of silver oxalate is of considerable interest because the course of the reaction can be profoundly modified by a variety of factors, each capable of being controlled so as to give reasonably reproducible results. It was pointed out by Macdonald and Hinshelwood (J., 1925, **127**, 2764) that specimens prepared with an excess of sodium oxalate decomposed much more quickly than those in which silver nitrate was in excess at precipitation; and that oxygen exerted a strong retarding influence. It has now been found that there are other modifying factors : that the dispersion of the precipitate in an oil or in molten wax slows down the reaction in a curious manner; that dispersing it in gelatin has a similar but less pronounced effect; and that mercury vapour produces acceleration. It was hoped that a close stndy of the decomposition under these different conditions would throw light on the mechanism of the reaction.

EXPERIMENTAL.

Preparation and Description of Specimens.—Fourteen specimens were prepared by precipitation from known concentrations of sodium oxalate and silver nitrate. The reagents were of analytical quality and were used without further purification. Precipitation was carried out with solutions of from $N/5$ to $N/500$, and one reagent was kept in excess the whole time except in one case, where an effort was made to keep the concentrations equivalent throughout. The specimens were washed from six to twelve times by decantation, filtered, and again washed. After drying in a vacuum desiccator, they were stored in the dark. During the preparation, light was excluded as far as was consistent with work in the open laboratory. The results obtained by this procedure were only approximately reproducible. Since the precipitate is of a semi-colloidal nature, it is probable that exact duplication of a specimen could not possibly be obtained unless the temperature, rate of stirring, and time of washing were controlled. Further, the preparations should be made and weighed out under photographic dark-room conditions.

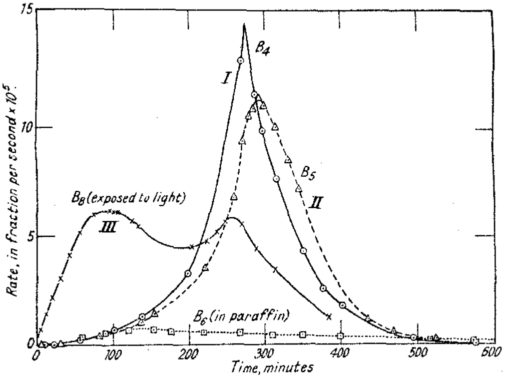
The substance prepared by the above method was microcrystalline, the average diameter of a single crystal being about 3×10^{-4} cm. The specimens with a considerable excess of either component had the smaller and more regularly sized crystals. (In all cases, however, some of the smallest crystals were lost in the process of filtration and washing.) Large crystals were also prepared, and by two methods : (1) 1 g. of oxalate was recrystallised from 45 l. of water by evaporatiou in a vacuum at 50° (slight decomposition had evidently taken place during manufacture, the crystals being somewhat discoloured); (2) an ammoniacal solution of the oxalate was evaporated, giving very imperfect crystals 1—3 mm. long, and affording a large proportion in irregular thin plates which floated on the mother-liquor until pushed under the surface. This flotation was an example of a phenomenon observed generally, *viz.*, that the substance resisted wetting by water.

The crystals obtained from the ammoniacal solution were examined by Dr. F. Walker, of the Geology Department, who reports that they are either monoclinic or triclinic, with an extinction angle (ZAc) of 16°, and a refractive index considerably greater than that of methylene iodide (1·72); and that there are two very well-defined cleavages at 83° to one another.

According to the I.C.T., the density of silver oxalate is 5·029, and its heat of decomposition 29,150 cals. per mol.

Measurements.—It is possible to measure either the quantity of carbon dioxide evolved or its rate of evolution. Both determinations may be required in the subsequent analysis, and since the process of graphical integration is much more accurate than that of graphical differentiation, the rate of decomposition was always measured directly. The method employed was a modification of that described in the earlier paper for decompositions in a vacuum, which gives directly the rate of reaction in arbitrary units. Briefly, the sample, usually weighing 0·01—0·02 g., was placed in a small bulb attached to a McLeod gauge and a vacuum train, and heated at constant temperature. Connection with the pumps was cut off periodically, and the rise of pressure in a measured short time (about 1 min.) was determined by the McLeod gauge. In order to start the reaction with the minimum time-lag, the bulb was pivoted on a ground-glass joint, so that it could be plunged into the previously adjusted oil thermostat. In the most rapid experiments, a differential manometer was substituted for the McLeod gauge, and the rate was measured by the

Fig. 1.



Decomposition of specimen B (excess oxalate) by three methods at 110°. *Curves I and II show the degree of reproducibility attained in experiments carried out (in a vacuum) under identical conditions.*

time taken by the mercury to rise between two etched marks about 1 mm. apart. By this means, as many as four readings could sometimes be taken in one minute.

The rates are thus obtained in arbitrary units, which depend on the weight of the sample taken and the dimensions of the apparatus. They were converted into standard units by the following method. At the end of the experiment, the amount of any unchanged oxalate was estimated by attaching the sample to a micro-gas-burette and heating it strongly. The rate–time curve was then plotted, and integrated by square-counting, so that the area which corresponded to 100% decomposition could be determined. By dividing the observed rates by the area and multiplying by a constant factor, depending on the scale of the graph, the rates in units of *fraction per second* were found. This is the unit which is used throughout.

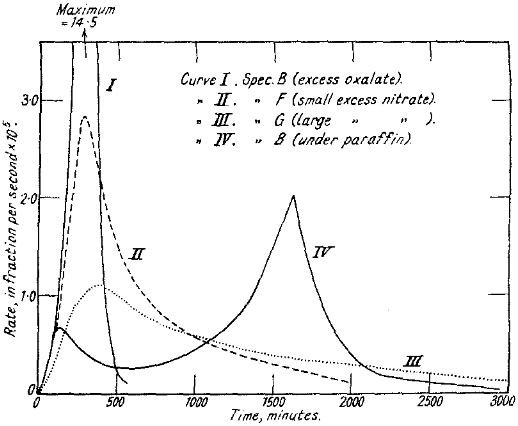
The general trend of nearly all the experiments is that which is typical of a large number of solid decompositions. The rate is very low at the outset, accelerates to a pronounced maximum, and finally falls off, frequently giving an approximately symmetrical curve. A striking feature, however, and one which appears to be not uncommon in reactions of this type, is the variable behaviour of different samples of the same specimen. Although in general each run was characteristic of the particular preparation used, it was found impossible to duplicate exactly any curve, and variations in the maximum rate of up to 20% were found. This is illustrated by Curves I and II (Fig. 1), which show two runs with specimen *B* under identical conditions, and these

should be compared with Curves I, II, and III (Fig. 2), which show runs with three different preparations. (All curves drawn to the same scale enclose equal areas, representing 100% decomposition.)

In assessing the importance of these variations, it must be remembered that the decomposition is strongly autocatalytic, and that such a reaction is dependent on, and extremely sensitive to, traces of the reaction product that may be present at the outset. On the other hand, the differences which may be expected to exist between individual crystals cannot in this case affect the result, since approximately 10^8 micro-crystals were decomposed together in each run, and the chance factors associated with the different units must have averaged out. In attempts to trace the variations to some controllable factor, about 30 runs were made under different conditions, mostly with one specimen (*C*). The results of this investigation were mainly negative, and are summarised as follows.

(1) The earlier runs had been conducted at 131°, and it seemed possible that at this temperature self-heating might cause irregularities. Temperatures down to 86° were therefore employed, without any improvement being noticeable. Nevertheless, a temperature of 110° was thereafter employed normally. It has since been found that the self-heating effect enters into the decomposition of the more unstable specimens at 131°, but that it does not affect the early stage of the decomposition, which is the seat of the irregular behaviour.

Fig. 2.



Showing the retarding influence of silver nitrate (Curves I, II, and III) and of paraffin (Curve IV) (Temp., 110°).

(2) It is known that air exerts a retarding influence, and it was therefore thought that variations in the hardness of the vacuum used might influence the reaction. This, and the possible effect of variations in the temperature of the thermostat, were therefore investigated by running the decompositions in pairs, a common vacuum system being used and the bulbs being immersed side by side in one thermostat.

(3) Adsorbed air and moisture were removed by 15 hours' evacuating at $< 10^{-5}$ mm., and comparative runs were made with long and with short evacuation.

(4) During the course of these experiments, it was observed that the presence of mercury in the reaction vessel (but not actually in contact with the salt) had a strong catalytic effect on the reaction, and a similar acceleration due to sulphur compounds has been reported by Sheppard and Vanselow (*J. Amer. Chem. Soc.*, 1930, 52, 3468). The possibility of accidental contamin-

ation by mercury vapour from the pumps and gauges, and of sulphur compounds from the gas used for sealing on the reaction vessel, was therefore investigated.

(5) It was found that strong exposure to ultra-violet light produced considerable acceleration (see p. 836). A specimen was therefore prepared, manipulated, and decomposed under photographic dark-room conditions.

It was clear that the variations were not due exclusively to any of the above factors, and little improvement resulted from the adoption of the precautions suggested by them.

(6) Lastly, it was thought that the decomposition might spread by infection from one crystal to the next (compare Pease and Taylor, *ibid.*, 1921, **43**, 2179, on the reduction of copper oxide by hydrogen). This would have explained the irregular behaviour of the samples, and also the fact that, as will be shown in Part II, an exponential term appears in the analysis of the curves. It was tested by conducting the decomposition under molten paraffin wax (purified by boiling with alkali) or under oil (Cenco pump oil, No. 11032), and also by making a suspension of the oxalate in gelatin, after the manner of a photographic " emulsion." The decomposition in gelatin proved to be very similar to that in a vacuum, which effectively disposed of the hypothesis. The course of the decomposition under paraffin was, however, unexpected. The significance of the curves obtained, one of which is illustrated in Fig. 2, Curve IV, will be discussed later. At present it is sufficient to state that the experiments under wax or oil gave no higher degree of reproducibility than those in a vacuum.

It is probable that the cause of the discrepancies lies in the accidental production of nuclei prior to the beginning of the reaction. From the above experiments it would seem that these were mostly formed by mechanical damage to the sample during manipulation (it is known that quite light grinding causes marked acceleration), but that in some cases exposure to light was a contribntory factor. This view is supported by the results obtained by other workers in the same field, who have, in general, found that reproducible results can only be obtained by previously treating the sample in a way which may be expected to lead to the formation of a constant number of nuclei. Another possible cause of variation, however, lies in the fact that the small portion of each sample in actual contact with the walls of the vessel attained the temperature of the bath much more rapidly than the bulk of the compound which, since the decompositions were carried out in a hard vacuum, were heated only by radiation.

A correction which takes account of this slow heating of the bulk of the sample has to be applied to the observed time and to the first few rate determinations. The necessary data were obtained from experiments in which a thermometer or a thermocouple was heated under the same conditions as the oxalate, and from the known temperature coefficient of the reaction. This correction had, of course, to be applied equally to all runs, and no account could be taken of variations in the size of the vessel, the thickness of its walls, the distribution of the solid, or the conducting effect of any gases liberated in the course of the reaction. An idea of the magnitude of the correction will be obtained from the fact that, at 131°, 7·5 mins. had to be subtracted from all times over 15 mins. In these cases, the maximum rate was reached in times varying between 22 mins. and 60 mins. from the start of the reactiou, so that little reliance can be placed on observations made at this temperature, unless they are confirmed by those made at a lower temperature where the correction is relatively of much less importance. The results indicated that in some cases the correction applied was too large. That it is of the right order can be shown by a simple calculation based on the rate of heating of a blackened sphere by radiation.

When the decomposition was carried out in air or under a liquid, experiment showed that the necessary correction was negligible.

Results.

Effect of Ionic Concentration at Precipitation.—The method of preparation and some of the characteristics of the decomposition at 110° are given in the table. It will be seen that, in general, as the concentration of silver nitrate used is increased, so the maximum rate attained diminishes. It is clear that, of the ions normally present, it is the nitrate which is most effective in producing this result, for specimen *I*, though prepared with an excess of oxalate over silver, was rendered stable by the addition of a quantity of sodium nitrate. That the effect is not peculiar to the nitrate ion is clear from specimen *H*, in which silver sulphate was substituted for silver nitrate. The sulphate ion, indeed, seems to be more effective than the nitrate ion, and a specimen which was prepared in the presence of sulphuric acid (*J*) was extremely stable.

A study of the last three columns of the table, however, shows that the results are not at all simple. The decrease in the maximum rate which is associated with an increase in the nitrate-ion concentration is caused by two factors: (i) a general slowing down of the reaction, as indi-

TABLE.

Showing the method of preparation of the various specimens and the chief characteristics of their decomposition at 110°. (Results for specimens marked with an asterisk are calculated from experiments at about 131° by the use of a temperature coefficient of 3·0 for 10°.) In specimens *C*, *D*, and *E*, the two salts were added simultaneously to 100 c.c. of water. In all other cases the solutions were mixed in the order given. The first 12 specimens are arranged in order of increasing nitrate-ion concentration.

Spec.	Method of preparation.	Rate at max. $\times 10^5$.	Time at max. (mins.).	% at max.	Time at 90% (mins.).
O	2000 C.c. $N/5$-$Na_2C_2O_4$ + 25 c.c. $N/5$-$AgNO_3$	16·2	207	30·9	640
Q	2000 C.c. $N/20$-$Na_2C_2O_4$ + 25 c.c. $N/5$-$AgNO_3$	10·9	270	43·8	464
P	500 C.c. $N/20$-$Na_2C_2O_4$ + 25 c.c. $N/5$-$AgNO_3$	13·7	280	48·0	363
B	500 C.c. $N/5$-$Na_2C_2O_4$ + 600 c.c. $N/60$-$AgNO_3$	12·6	281	42·4	388
M	40 C.c. $N/20$-$Na_2C_2O_4$ + 20 c.c. $N/20$-$AgNO_3$ + 1 c.c. of 0·03% soluble fluorescein	5·08	230	38·0	570
A	500 C.c. $N/5$-$Na_2C_2O_4$ + 50 c.c. $N/5$-$AgNO_3$	6·85	319	42·6	550
C	203 C.c. $N/20$-$Na_2C_2O_4$ + 200 c.c. $N/20$-$AgNO_3$ + 100 c.c. H_2O	4·30	395	44·6	699
D	200 C.c. $N/20$-$Na_2C_2O_4$ + 200 c.c. $N/20$-$AgNO_3$ + 100 c.c. H_2O	3·88	379	43·7	735
E	203 C.c. $N/20$-$AgNO_3$ + 200 c.c. $N/20$-$Na_2C_2O_4$ + 100 c.c. H_2O	2·94	535	45·1	910
F	500 C.c. $N/5$-$AgNO_3$ + 600 c.c. $N/60$-$Na_2C_2O_4$	2·74	295	21·8	1500
G	500 C.c. $N/5$-$AgNO_3$ + 50 c.c. $N/5$-$Na_2C_2O_4$	1·16	375	15·5	4370
**I*	250 C.c. $N/20$-$Na_2C_2O_4$ + 50 c.c. $N/20$-$AgNO_3$ + 8·5 g. $NaNO_3$	0·56	562	5	(5600) [1]
**H*	500 C.c. $N/20$-Ag_2SO_4 + 50 c.c. $N/20$-$Na_2C_2O_4$	4·6	562	54	1820
**Am* (1)	Recrystallised from ammonia	5·4	239	15·5	1025
**Am* (2)	Recrystallised from ammonia	8·7	251	35·0	674
K	Recrystallised from water	1·56	360	13·8	—

[1] Approximate value, by extrapolation.

cated by the longer time elapsing before the maximum rate is reached; and (ii) the fact that this maximum is in some cases attained when a much smaller proportion of the substance has decomposed. In this connection, specimens *F*, *G*, and *I* are particularly instructive. The last column shows that with the exception of specimens *O* and *Q*, the time of 90% decomposition increases with the nitrate-ion concentration, *i.e.*, the tail of the curve is much extended. Some of these points are illustrated in Curves I, II, and III (Fig. 2).

The last three specimens in the table consist of large crystals. The figures show that the decomposition of these is similar to that of a precipitate prepared with a slight excess of silver nitrate.

Effect of Air.—Accurate measurements of the rate of reaction in the presence of air are not easy to carry out, since normally the carbon dioxide produced in the course of the reaction tends to displace the air in the neighbourhood of the crystals. A few experiments were, however, attempted, and these indicated that up to about 3% decomposition the reaction followed the same course as in a vacuum, but that thereafter, instead of continuing to accelerate, the rate decreased progressively.

Effect of Paraffin.—The result of decomposing the oxalate under molten paraffin wax is shown in Fig. 2, Curve IV. It will be seen that, as in air, the decomposition follows the same course as in a vacuum for a time equivalent to about 3% decomposition, and that the velocity then falls. Instead of continuing to fall, however, it rises again to a second and greater maximum. Irregular bumps were frequently observed around this second maximum, and to a less extent in the intermediate period of low velocity. The curve illustrated is for specimen *B*, precipitated with excess oxalate. The curve for specimen *G* (excess nitrate) under paraffin was similar, the only notable difference being that the first maximum represented only about one-third of the velocity found for *B*. It was not possible to differentiate between the second acceleration in the two cases.

Effect of Exposure to Light.—When specimen *B* was irradiated for 6 mins. by the light of a quartz mercury-vapour lamp, consuming 300 watts, and was subsequently decomposed under paraffin, the rate at the first maximum was doubled, but the curve was otherwise unaltered. Similarly, the specimen prepared and manipulated in the dark gave a smaller first maximum, though this may be due, in part at least, to the fact that the crystals of the precipitate were considerably smaller. Curve III, Fig. 1, exhibits the result of decomposing an irradiated sample of specimen *B* in a vacuum: the initial velocity has been greatly increased, and a curve with two

maxima is obtained. The times of these two maxima make it evident that the first corresponds to the first maximum in paraffin, and the second to the normal maximum of a vacuum decomposition. A close examination of the curves obtained for the decomposition in a vacuum of the unexposed samples shows that there is always a slight hump present in the curve corresponding in time to the first maximum in paraffin, and that the effect of the action of light is to increase this very greatly. The size of the hump varies a good deal from one specimen to another, and in general increases with the age of the sample.

Microscopic Examination.—Crystals of the precipitate are too small for detailed examination even under the highest magnification, but it can be seen that at no time is there any great difference between one crystal and its neighbours. The decomposition, as indicated by a gradual darkening in colour, starts immediately in all particles. There is no evidence whatever of a spread of the reaction from one crystal to another. Examination of the large crystals shows that these darken through reddish-brown to opacity (5—10% decomposition), after which no change is observable, the final mass of silver being a pseudomorph of the original crystal of oxalate. The darkening appears to be quite uniform throughout the mass of the crystal, *i.e.*, it is proportional to the thickness of the crystal at any point. It clearly does not proceed on the surface, as does the decomposition of copper sulphate pentahydrate (Garner and Tanner, J., 1930, 47; Hume and Colvin, *Proc. Roy. Soc.*, *A*, 1931, **132**, 548), nor does it spread from a few isolated nuclei as in potassium chlorate (Coppock, Colvin, and Hume, *Trans. Faraday Soc.*, 1931, **27**, 283).

Discussion.

It has previously been suggested (Macdonald and Hinshelwood, *loc. cit.*) that the decomposition is controlled by the formation and growth of nuclei of reaction product in the crystal. Benton and Cunningham (*J. Amer. Chem. Soc.*, 1935, **57**, 2227), who studied quantitatively the effect of light on the reaction, concluded that irradiation increases the number of nuclei present at the start. This conclusion is fully borne out by the experiments described above. The whole reaction is, however, somewhat more complex than these investigators realised, and changes in the shape of the curve follow upon alterations in the conditions in a manner which cannot be explained on the hypotheses which they put forward.

It will be clear from the foregoing description that there are several distinct modes of decomposition which can be more or less isolated from one another experimentally. It will be convenient to refer to such modes of decomposition as " processes." Their more obvious characteristics are summarised below.

The first, Process I, is best represented by the first maximum in paraffin. It normally accounts for not more than 5% of the reaction, but this amount can be greatly increased by exposure to light. The similarity of the first few per cent. of the decompositions in paraffin, in a vacuum, in air, and with various ionic concentrations at precipitation, shows that Process I is unaffected by any of these conditions. It is almost certain, therefore, that it consists in the decomposition of nuclei which are present at the outset of the reaction, and that each nucleus can account for the decomposition of only a small fraction of the crystal. The alternative explanation, that only a few of the crystals possess nuclei, is disproved by the microscopic examination of the partially decomposed substance.

Process II is actively operative in the decomposition of the more unstable specimens in a vacuum. It is quite distinct from Process I, as is shown by the double maximum obtained when the sample has been irradiated, and by the fact that it may be reduced by increasing the concentration of nitrate ion and entirely eliminated by carrying out the reaction under paraffin or in air. Its sensitivity to the environment proves that it is essentially a surface reaction, and is thus connected with the formation of fresh nuclei.

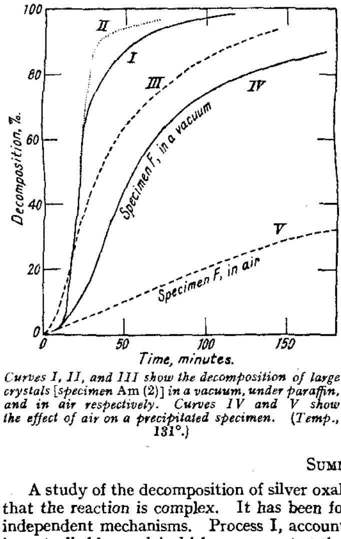
The reaction which causes the second maximum in paraffin is Process III. This is apparently not so sensitive to environment as Process II, since it is not affected by the ionic condition of the surface. It is uncertain to what extent it is present in the decomposition of ion-retarded specimens in a vacuum, or in the decompositions in air.

The above processes are all of an accelerating type. It is probable that a fourth process is present, which controls the long period of decreasing velocity found in experiments in air, and with ion-retarded specimens; but it has not yet been possible to isolate this

sufficiently from the other processes to enable any theory as to its nature to be put forward.

Finally, important evidence as to the nature of the reaction is obtained from the decomposition of large crystals. It has been seen that, when decomposed in a vacuum, these gave curves similar to those found for precipitated specimens. This indicates that the unit of decomposition is not the crystal as a whole, but the " crystallite " of which all large crystals are supposed to be made up (see Garner and Hailes, *Proc. Roy. Soc.*, *A*, 1933, **139**, 576). If we assume that the micro-crystals which comprise the precipitate consist of single crystallites, or contain, at most, a few, and that the large crystals contain many, then the only real difference between the two types will be that the external surfaces of the micro-crystals will become " internal surfaces " in the macro-crystals. Now when the large crystals are decomposed under paraffin, the course of the decomposition is found to be almost exactly the same as in a vacuum (Fig. 3, Curves I and II). The explanation is clear. Process II, which is the one affected by paraffin, is associated with the surfaces of the crystallites. In the case of a precipitate, these are the external surfaces, and are accessible to the paraffin; whereas in the case of large crystals, they are internal surfaces to which the paraffin is unable to penetrate, and whose decomposition is therefore unaffected by the medium in which the crystal is placed. Similarly, air, which also eliminates Process II, has little effect on the large crystals (Curve III, Fig. 3). In the latter case, however, the isolation of the inner surfaces is not so complete, and the reaction is retarded to a certain extent. It must be remembered that carbon dioxide is able to diffuse out of the crystal without disrupting it, and it is by no means unlikely that air is able to pass in by the same channels.

FIG. 3.



Curves I, II, and III show the decomposition of large crystals [*specimen* Am (2)] *in a vacuum, under paraffin, and in air respectively. Curves IV and V show the effect of air on a precipitated specimen.* (*Temp.*, 131°.)

The hypothesis that the crystallite is the unit of decomposition is in accord with the appearance of the large crystals when observed under the microscope.

SUMMARY.

A study of the decomposition of silver oxalate under a variety of conditions has proved that the reaction is complex. It has been found possible to isolate experimentally three independent mechanisms. Process I, accounting normally for about 3% of the reaction, is controlled by nuclei which are present at the outset, and whose number may be increased by various means. Process II, which normally accounts for the remainder of the reaction, is very sensitive to the conditions at the surfaces of the crystals (or, in the case of large crystals, of the component crystallites). When Process II is suppressed by conducting the decomposition under paraffin, Process III becomes prominent.

It has further been shown that the crystals of the precipitate or the crystallites of large crystals decompose as independent units unaffected by their neighbours.

THE UNIVERSITY, ST. ANDREWS. [*Received, February 1st*, 1936.]

194. *The Thermal Decomposition of Silver Oxalate. Part II. Theoretical.*

By J. Y. Macdonald.

A more detailed analysis of the rate-time curves obtained during the decomposition of silver oxalate under various conditions (preceding paper) has now been made and theories are suggested as to the nature of the mechanisms which are believed to be taking part.

As the reaction is complex, it is not surprising that none of the simple equations suggested for such solid decompositions offers a complete explanation of the experimental results (see, *e.g.*, Lewis, *Z. physikal. Chem.*, 1905, **52**, 310; Centnerszwer and Bružs, *ibid.*, 1926, **119**, 405; Roginski and Schulz, *ibid.*, 1928, **138**, 21; Topley and Hume, *Proc. Roy. Soc.*, 1928, *A*, **120**, 211).

There appears to be no reason for departing from the hypothesis put forward by Macdonald and Hinshelwood (J., 1925, **127**, 2764), *viz.*, that the reaction is governed by the formation and growth, in the crystal, of nuclei of the reaction product. Quite apart from other considerations, this seems to be the only theory which is sufficiently adaptable to meet the necessary requirements. Since that theory was published, the spread of a reaction from small nuclei has been observed and photographed in several cases (Kohlschütter, *Kolloid-Z.*, 1927, **42**, 254; Coppock, Colvin, and Hume, *Trans. Faraday Soc.*, 1931, **27**, 283; Garner and Southon, J., 1935, 1705). Topley and Hume (*loc. cit.*) were the first to deduce equations for this mechanism, taking two special cases: (i) where one nucleus was present on each crystal at the outset, and (ii) where the whole surface became rapidly covered with nuclei. Contributions on the same lines have been made by others, notably Garner and his co-workers (J., 1930, 47; 1931, 2123; 1933, 1393, 1398; 1934, 720; *Proc. Roy. Soc.*, 1933, *A*, **139**, 576). There seems to be little doubt that most non-explosive solid decompositions follow some modification of this mechanism, and are therefore essentially autocatalytic, proceeding at the interface between the original solid and the product of the reaction. Obviously, as the nuclei increase in size and number, so, in general, will the area of the interface increase, and with it the rate of reaction. When a certain fraction of the compound, which seldom greatly exceeds 50%, has decomposed, the growing nuclei interfere with one another, and the regions where decomposition first began become exhausted. The rate of the reaction will therefore pass through a maximum and finally fall to zero. It will be seen that the hypothesis gives a good qualitative description of the results reported in the previous paper.

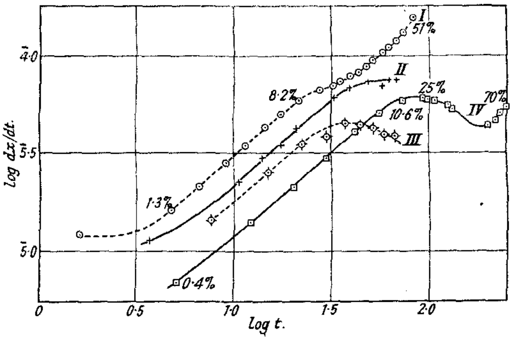
A more detailed examination of the curves obtained in this and certain analogous decompositions, however, reveals a serious difficulty, *viz.*, that in many cases the decomposition follows an exponential law up to the maximum rate (with which portion of the curve alone this paper is concerned). Now, on the simplest hypothesis, which is that the linear rate of propagation of the reaction is constant and that the reaction spreads in all three dimensions so that the growing nucleus assumes a solid form, no such exponential equation can be deduced. The course actually followed is reminiscent of the familiar " branching chain " mechanism (see Semenoff, " Chain Reactions "), and Garner (*loc. cit.*) has investigated the possibility of the formation of linear chains of molecules, and of chains of crystallites, each of which decomposes rapidly compared with the time taken for the reaction to spread from one to another. In the present instance, it has been shown (Part I) that the reaction does not spread from one crystallite to another, and the cause of the exponential term must be sought in the decomposition of the individual crystallites. Let us examine, therefore, as simply as possible, the various ways in which a single crystallite may decompose, on the assumption that the number of nuclei on each is not very great. We may conveniently divide the possibilities into three groups, according to the " shape " which the nucleus assumes on growth.

The first is that in which the reaction tends to proceed in the form of linear chains, *i.e.*, each nucleus grows in one dimension only. There are here three possibilities. (*a*) The reaction proceeds solely from the n nuclei present initially. If K be the rate of linear ad-

vance of the reaction, the total rate of reaction will be constant ($= Kn$). This mechanism can only account for the decomposition of a very small fraction of the crystal, *viz.*, n/(the number of molecules on one crystal face). (*b*) Fresh nuclei may be formed spontaneously. In the simplest case these would be formed at a rate proportional to the area of the undecomposed oxalate, and at the outset of the reaction this would be virtually constant. The total rate of reaction would then be proportional to t, so long as the first chains to be formed were still active. This mechanism may be combined with (*a*) to give an equation of the type $dx/dt = Kn + K't$. (*c*) The chains may branch in the crystal. As we have seen, the reaction will then follow an exponential law.

In the second group, the reaction is to be considered as spreading in two dimensions along the planes of the crystal; *i.e.*, the nuclei grow in the form of thin plates. Such nuclei have recently been observed by Garner and Southon (*loc. cit.*). They may, within limits, be of any thickness, but we shall consider only the simplest case, *viz.*, that the layer has a depth of only two atoms of silver, this being the product of the decomposition of one molecule of oxalate. It is found that, if the reaction proceeds entirely from the nuclei originally

Fig. 1.



Curve I.—Spec. S, in Gelatin, 131°. Curve II.—G, in vac., 131° (nitrate excess). Curve III.—F, in air, 131°. Curve IV.—B, exposed to light, 110° (in vac.).

present, the rate will be proportional to the circumference of the plates, *i.e.*, to the first power of t, and that this mechanism can account for the decomposition of a fraction of the whole equal to n/(the number of molecules on one crystal edge), *viz.*, the fraction of the total number of planes which possess nuclei. The spontaneous generation of nuclei will now give a rate of reaction which, in the simplest case, is proportional to the second power of t, and again, branching of the planes may take place, giving, as before, an exponential equation. It is to be expected that in the later stages of the reaction the rate will fall somewhat below the theoretical, on account of interference between the planes.

In the third group, the reaction spreads in three dimensions, though not necessarily at an equal rate along each. There are here only two possibilities: that the reaction proceeds from a fixed number of nuclei, or that the nuclei are generated spontaneously. This is the type of reaction considered by Topley and Hume (*loc. cit.*) and by Bentou and Cunningham (*J. Amer. Chem. Soc.*, **1935**, *57*, 2227). The reaction will be proportional to the second or third power of t according to whether fresh nuclei are formed or not, and again, the rate will tend to fall below the theoretical as the decomposition proceeds. It has already been noted that branching, and therefore an exponential type of equation, cannot occur in this case.

It is clear that the above considerations will be valid only for a time equal to that taken by a single nucleus to complete its decomposition.

The experimental results may be tested in the light of the foregoing discussion by plotting log dx/dt against log t (dx/dt being the observed rate of reaction). In every case except where branching occurs, a straight line should be obtained from which the constants of the equation

$$dx/dt = kt^m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

can be read off.

Process I.—It was shown in Part I that at least three different mechanisms are required to determine the complete decomposition. One of these, Process I, normally accounts for only about 3% of the reaction. This amount, however, can be increased by just those manipulations (grinding and exposure to light) which may be expected to lead to an increase in the number of nuclei. It can be isolated from Process II in a number of ways.

In Fig. 1, log dx/dt is plotted against log t for four experiments in which Process I predominates. In Curves I, II, and III, Process II has been suppressed by gelatin, by ionic adsorption, and by air, respectively, while in Curve IV, Process I has been greatly stimulated by exposing the sample to ultra-violet light. It will be seen that a good straight line is obtained over a fair range, and that the slope of the line is approximately equal to unity. Table I gives a complete list of the values of m found in all experiments in which Process I

TABLE I.

Expt.	Method.	Temp.	m.	$10^8 k_1$.	$10^9 k_2$.	$10^4 C$.
B 16	(p)	100°	(1·25)	0·25	4·45	0·845
B 6	(p)	110	(1·00)	5·75	57·5	3·40
B 9	*(p)*	*110*	*(1·20)*	*1·91*	*30·3*	*2·08*
B 10	(p)	110	(1·07)	4·57	53·8	3·04
B 8	(v), (i)	110	0·83	182	1230	22·7
R 1	(p)	110	(1·00)	3·6	36·0	2·69
F 8	(v)	110	(1·15)	3·47	49·0	2·69
G 5	(p)	110	(1·26)	0·71	12·9	1·36
G 6	(p)	110	(0·97)	3·55	33·1	2·66
G 3	*(v)*	*110*	*1·32*	*0·72*	*15·1*	*1·40*
G 4	(v)	110	1·30	0·83	16·5	1·45
B 11	(p)	120	1·34	15·9	348	5·32
B 12	(p)	120	1·10	31·6	400	7·94
B 14	(oil)	120	(1·31)	13·8	282	5·00
B 19	(p), (i)	120	1·07	93·3	1090	13·05
B 15	(p)	130	1·00	229	2290	21·41
F 1	(v)	131	1·32	219	4580	16·41
F 2	(air)	132	0·82	282	1860	29·11
G 2	(v)	131	0·79	363	2240	34·83
I 1	(v)	132	(1·00)	135	1350	16·48
S 1	(g)	131·2	0·84	444	3070	32·06
S 2	(g)	131·2	0·73	740	4080	57·28
H 1	(v)	131	(1·15)	490	6910	27·42
J 1	(v)	130	0·87	3·6	26·7	2·66

Mean value of $m = 1·05 \pm 0·035$.

(p) in paraffin; (v) in a vacuum; (g) gelatin emulsion; (i) irradiated by ultra-violet light.

is expected to predominate. The values in parentheses indicate either that few observations were obtained over the significant portion of the curve or that the points do not fall very close to a straight line. Such values have been given half weight in the mean, which was found to be **1·05 ± 0·03**. The closeness of this value to a whole number is doubtless partly accidental. As has been explained, one would expect the experimental value of m to fall somewhat below the theoretical value. On the other hand, in many of the experiments quoted, Process II has not been completely suppressed, and this would tend to raise the value again, thus counterbalancing the previous error. There seems little doubt, however, that the fundamental equation of Process I is

$$dx/dt = kt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

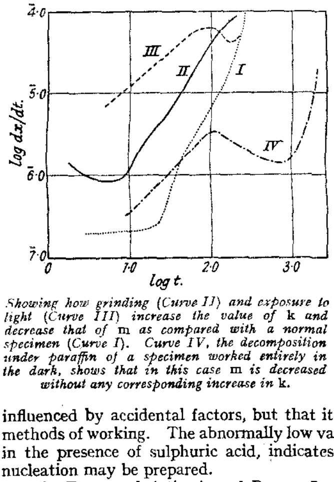
This conclusion seems to be in agreement with the experiments of Benton and Cunningham (*loc. cit.*), who, studying the effect of light on a specimen of silver oxalate prepared with a small excess of sodium oxalate, found that exposure to light increased the value of

k and decreased that of m [equation (1)], values as low as 0·4 being obtained with prolonged exposure. Their results and those of the present author both seem to be more in accord with equation (2) than with their equation, in which m, in the ideal case, would have the value 2 (see also Fig. 2).

On the assumptions which have been made, equation (2) could result only from one of two mechanisms: a linear chain reaction with the spontaneous generation of fresh chains, or a reaction which spreads in two dimensions from a fixed number of nuclei. It has been clearly demonstrated, however, that Process I is dependent on the presence of nuclei at the start. It would seem, therefore, to consist in the growth of planes of silver atoms through the lattice of the crystal, each plane starting from a point on the surface. It has already been noted that such a mechanism can account for the decomposition of only a small fraction of the compound, a conclusion which is in complete accord with experiment.

If this theory is correct, the value of k should give a measure of the number of nuclei present at the outset, provided that the rate of forward propagation of the reaction through the crystal is always the same at any temperature. Thus if the nuclei predominate at the edges of the crystals, the length of each advancing line will be that of one-quarter of the circumference of a circle of radius Kt, and the total rate of reaction will be $\frac{1}{2}\pi n K^2 t$, whence $k = \frac{1}{4}\pi n K^2$.

Fig. 2.



Showing how grinding (Curve II) and exposure to light (Curve III) increase the value of k *and decrease that of* m *as compared with a normal specimen (Curve I). Curve IV, the decomposition under paraffin of a specimen worked entirely in the dark, shows that in this case* m *is decreased without any corresponding increase in* k.

In Table I, cols. 5 and 6, are given the values of k_1 and k_2, the rates at 1 min. and at 10 mins. respectively, as read off the graph of log dx/dt against log t. Of these, k_2 ($= 600k$, if t is expressed in seconds) is probably the more accurate measure of k, since it avoids the extrapolation necessary for the determination of k_1 (which thus reflects any error in m). It will be seen that k_2 exhibits a greater constancy than k_1, that for normal experiments k is always of the same order of magnitude, but that it is greatly increased by irradiation with ultra-violet light, and that the differences between specimens are of the same order as those between different samples of the same specimen. This supports the view that nucleation is rather easily influenced by accidental factors, but that it cannot be entirely eliminated by the normal methods of working. The abnormally low value of k for specimen J, which was precipitated in the presence of sulphuric acid, indicates a method by which specimens resistant to nucleation may be prepared.

The Energy of Activation of Process I.—The temperature coefficient of the primary reaction, and hence the energy of activation, may be determined in a number of ways. The most direct method is that of Topley and Hume (*loc. cit.*), in which the temperature is altered rapidly to a new value in the course of an experiment. The number of nuclei and the total interfacial area are the same immediately before and after the alteration, as is shown by the return of the rate of decomposition to the normal value on restoring the original temperature. The ratio of the rates at the two temperatures is thus the ratio of the rates of forward propagation of the reaction. The method is not particularly accurate unless the rate of reaction is constant over the time of the experiment, but it serves as a useful check on the other methods. A single determination between 130·5° and 136° gave a value of $E = 38{,}500$ cals., whereas the average of three determinations by Benton and Cunningham between 117° and 100° gives $E = 25{,}400$ cals. (These workers calculate a value of 8,500 cals. from the same data, but this seems to be due to a misunderstanding of the principle of the method.)

The energy of activation may also be calculated from the data in Table I, and by two methods, if it be assumed that the initial number of nuclei is independent of temperature. In the first method the rates are compared at such times that equal fractions of the oxalate (x) have decomposed, so that the total area of the advancing interface is the same in all cases. The required factor is obtained by integrating equation (1) :

$$x = kt^{(m+1)}/(m + 1) + \text{constant}.$$

The constant disappears if we assume that the true initial rate is vanishingly small, whence

$$t_x = [x(m + 1)/k]^{1/(m+1)}$$

and $$(dx/dt)_x = kt_x^m = [kx^m(m + 1)^m]^{1/(m+1)}$$

The values of $C = [k_1(m + 1)^m]^{1/(m+1)}$ are given in the last column of Table 1. By taking all the values for normal experiments, and treating the variations as random errors, it is found that $E = 35{,}6000 \pm 1{,}610$ cals.

The second method is to put $k_2 = 300\pi nK^2$ in accordance with the theory outlined in the preceding section, whence $K \propto \sqrt{k_2}$. This is equivalent to assuming that the individual values of m are slightly in error, and should really equal unity. It gives $E = 32{,}700 \pm 1{,}160$ cals., which is probably the most accurate of the values, and its agreement with the other determinations is strong evidence in favour of the assumptions on which it is based. It is equivalent to a temperature coefficient of about 3·2 for 10°.

It is noteworthy that mercury fulminate, which decomposes at a comparable rate at the same temperature, has an energy of activation of 30,000 cals. (Garner and Hailes, *loc. cit.*).

Process II.—When we examine the decompositions in a vacuum of the specimens which are not retarded by ionic adsorption, and also the later portions of the experiments which are conducted under paraffin or in gelatin, we find that equation (2) no longer holds, but that the value of m increases with time up to a high figure. This is shown by the curve for specimen B (Curve I, Fig. 2), which is typical of many runs. The phenomenon is independent of temperature, and the curves at different temperatures can be derived from one another by altering the origin 0·5 logarithmic unit along both axes for each 10°, corresponding to a coefficient of 3·2. The shape of the upper portion of this curve suggests that the equation is now of an exponential type, *viz.*,

$$dx/dt = ae^{pt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The curve for the second acceleration in paraffin is approximately parallel to the corresponding portion of the decomposition in a vacuum (Curve IV, Fig. 2).

TABLE II.

Specimen.	log [NO_3'].	$p \times 10^4$. 96°.	100°.	106°.	110°.	117°.	120°.	131°.	Temp. coeff.
Am. (2)	—	—	—	—	—	—	—	71·0	—
O	−2·607	—	—	—	3·54	—	—	—	—
Q	−2·607	—	—	—	3·26	—	—	30·3	2·93
B	−2·041	—	1·07	—	2·82	—	6·35	27·4	2·75
P	−2·022	—	—	—	3·10	—	—	31·8	2·92
A	−1·744	—	—	1·22	2·15	—	—	21·6	2·97
C	−1·701	0·246	—	0·72	1·90	3·73	—	15·2	3·27
D	−1·699	—	—	—	2·22	—	—	—	—
E	−1·695	—	—	—	1·22	—	—	—	—
F	−1·041	—	—	—	1·88	—	—	13·3	2·54
S 1 (in gelatin)	—	—	—	—	—	—	—	2·6	—
B (in paraffin)	—	—	—	—	0·612	—	—	—	—
									Mean 2·90 ± 0·23

Plots of log dx/dt against t show that, although the reaction is somewhat more complex than represented above, a sufficiently close approximation to a straight line is obtained over such a considerable period as to suggest that equation (3) represents a fundamental mechan-

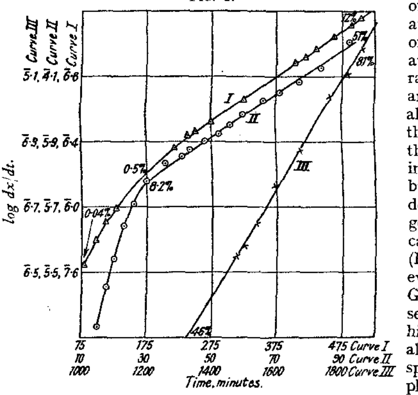
TABLE III.

Specimen.	$a \times 10^{8}$. 100°.	110°.	117°.	120°.	131°.	Temp. coeff.
Am (2)	—	—	—	—	16·4	—
O	—	1·89	—	—	—	—
Q	—	1·11	—	—	13·92	3·03
B	0·56	1·29	—	4·46	12·74	2·76
P	—	1·14	—	—	14·96	3·50
A	—	1·79	—	—	18·5	2·89
C	—	1·62	4·30	—	19·3	3·25
D	—	1·71	—	—	—	—
E	—	1·25	—	—	—	—
F	—	2·11	—	—	25·6	3·28
S 1 (in gelatin)	—	—	—	—	42·9	—
B (in paraffin)	—	0·149	—	—	—	—
						Mean 3·12 ± 0·24

ism of the reaction. The constants of this equation are given in Tables II and III, and examples of three experiments in Fig. 3.

This exponential equation indicates a mechanism quite different from the one discussed in the previous section. There seem to be but two possibilities—either that it is due to self-heating, the rate of evolution of heat being greater than the rate at which it can be conducted away, or that new nuclei are being formed at a rate which is a function of the rate of decomposition or of the amount of reaction which has already taken place. The first of these explanations is ruled out by the observation that the effect is independent of temperature, and by the fact that it appears in the decompositions in paraffin and in gelatin, where the heat generated can readily be conducted away (Fig. 3). It can be calculated, however, following the method of Garner and Hailes (*loc. cit.*), that self-heating may occur at the highest temperatures used, especially in the case of the more unstable specimens. This adequately explains an upward curvature in the plot of log dx/dt against t which is sometimes found in such cases, and care has been taken, in measuring the constants of Table II and III, to omit that portion of the curve where self-heating may be expected.

FIG. 3.



Curve I.—B 17, 100° *in a vacuum.*
Curve II.—S 1, 132° *in gelatin.*
Curve III.—B 6, 110° *in paraffin.*

The exponential character of this process seems, therefore, to be due to the formation of fresh nuclei, at a rate which is a function of the rate of decomposition. Now we have seen that the nuclei tend to grow in two dimensions, and that if such planes of reaction branch, the reaction will follow an exponential law. This is clearly the mechanism of Process II. We must therefore suppose that, at certain points on the decomposing planes, fresh planes of reaction start. That the points where branching occurs are confined to the surface of the crystal seems to be shown by the sensitiveness of Process II to external influences, such as the presence of air, of paraffin, and of adsorbed ions. Further, since the molecules *in the front line of the advance will be " hotter " than those immediately behind them,*

branching is most likely to occur at the point where this advancing line cuts the surface of the crystal. The rate of formation of fresh planes (dN/dt) will thus be proportional to the number of planes (N) in an active state, or $N = ne^{pt}$, where n is the number of nuclei at the outset of the reaction and p is the number of times a single plane of reaction divides per second.

Now if N' be the number of active nuclei at time τ, then the number of *new* nuclei formed between τ and $(\tau + d\tau)$ will be $pN' . d\tau = pne^{p\tau} . d\tau$. At time t, these will have been growing for $(t - \tau)$ seconds, and the sum of the lengths of the active boundaries of these nuclei will be

$$dr = \tfrac{1}{2}\pi K(t - \tau)pne^{p\tau} . d\tau$$

Integrating for all values between $\tau = 0$ and $\tau = t$, we find

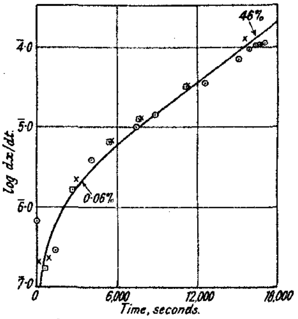
$$r = \tfrac{1}{2}\pi Kn[e^{pt} - (pt + 1)]/p$$

This gives the total interface due to nuclei formed since the beginning of the reaction. Adding to this the interfaces of the nuclei present at the outset ($\tfrac{1}{2}\pi Knt$) and multiplying by K, we find the measured rate of reaction

$$dx/dt = \tfrac{1}{2}\pi K^2n(e^{pt} - 1)/p \quad . \quad . \quad (4)$$

which is the required equation.

FIG. 4.



Showing three runs with specimen B in a vacuum at 110° compared with the theoretical equation. The line is drawn to the equation $dx/dt = 1{\cdot}29 \times 10^{-6}\, e^{0{\cdot}000107t}$.

□ *Expt.* B 3. × *Expt.* B 4. ○ *Expt.* B 5.

Attention should be directed to several points in connection with this equation. (i) It is based on the assumption that all planes of reaction product are actively growing at time t, and it will only hold good so long as the number of active planes is greatly in excess of those which have run their course. In practice, it holds well for the vacuum decomposition of specimens prepared with excess sodium oxalate, so long as these have not been greatly nucleated by artificial means. An example of the manner in which it can reproduce the experimental results is given in Fig. 4, in which the constants used are those found in Tables II and III, *i.e.*, the slope and intercept of the later portion of the curve. (ii) When the product pt is large, *i.e.*, in the later stages of the more strongly accelerating specimens, the equation approximates to equation (3). (iii) When pt is small, e^{pt} may be written $1 + pt$, and the equation reduces to equation (2), which, therefore, describes the decomposition of those preparations in which the rate of branching of the planes is small, as well as the early stages of all decompositions. (iv) The values of p (Table II) are roughly inversely proportional to the logarithm of the nitrate-ion concentration; *i.e.*, the rate of branching is dependent on the ionic condition of the surface. (v) The inverse proportionality which should exist between a (Table III) and p is largely obscured by the fact that, as can be seen from Table I, the values of n vary considerably from one sample to another. [a in equation (3) is equivalent to the term $\tfrac{1}{2}\pi K^2n/p$ of equation (4).] (vi) The temperature coefficient of p is not greater than that of a (and therefore than that of K). Now p is the rate of branching of the planes, and K is their linear rate of advance. The total number of divisions undergone by one plane in the course of its complete decomposition will therefore be proportional to p/K. Since this is almost independent of temperature, the extra energy required to start a fresh plane must be small, and division must take place whenever a suitable "bridge" is encountered.

These bridges may be permanent, and in the nature of surface discontinuities on the crystal. It seems more likely, however, that they consist of periodically recurring phase relationships between the atoms. It should be noted that the heat of reaction (29,150

cals.) is almost equal to the energy of activation. Reaction will take place if this heat be communicated to a neighbouring molecule at the moment when it is passing through its phase of minimum stability. The chance of branching taking place will therefore depend on the chance of such an energy transference taking place before the heat of reaction is dissipated in other directions. This, in turn, will depend on the presence, on the surface, of other molecules which may absorb the energy, such as nitrate ions and paraffin.

Process III.—Without some modification, the mechanism outlined above will not suffice to account for the results obtained under paraffin. First, it offers no explanation of the fall in velocity following the first maximum in the curve; and secondly, it is clear that as the total time of the reaction is much increased, it will no longer approximate to the time of decomposition of a single plane, so that the number of active planes will be only a small fraction of the total number of planes. These difficulties disappear if we assume that, in general, a plane may branch at any point along its edge. This is equivalent to assuming that nuclei may be formed spontaneously at the edges of the newly formed crystal blocks. As the reaction proceeds, these blocks become smaller, and the length of edge correspondingly greater. Thus the opportunity for the generation of fresh nuclei will increase with time. It must be supposed that this mechanism is active in the vacuum decompositions also, but that it is negligibly slow as compared with Process II. As explained above, the effect of paraffin is to remove the excess energy from the molecule in the front of the advancing plane, so that the leader behaves in no way differently from those behind.

In order to find the equation for this mechanism, it seems to be necessary to assume that the time of decomposition of a single plane is negligibly small compared with the total time of the reaction. Now, the first maximum in the curve is probably caused by the decomposition of the n nuclei present at the outset, and the maximum will correspond roughly with the time taken by a single plane to cross the crystal. For specimen B at 110°, this time is 138 mins., while the exponential portion of the second acceleration extends from 900 to 1800 mins. The assumption is therefore approximately correct.

If at time t the number of decomposed planes be N and if each of these gives rise to b new planes per second, then $dN/dt = bN$, and if w be the average number of molecules in one plane of the crystal, the total decomposition, x, is equal to wN, whence

$$dx/dt = w \, . \, dN/dt = WbN = bx$$

and

$$x = ce^{bt}$$

where c is the amount of reaction product at $t = 0$, which, if the original n planes decomposed instantaneously, would be wn. Differentiation gives

$$dx/dt = bwne^{bt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is an equation of the type found experimentally.

Numerical Calculations.—We are now in a position to evaluate the various constants which have been referred to. The following data are for specimen B at 110°.

We have already assumed that the time of the first maximum in paraffin is approximately equal to the time taken for the reaction to cross the crystal. The average size of a crystal of specimen B is $(1{\cdot}7 \times 10^{-4})^3$ c.c. From this, one may calculate that there are 1×10^{11} molecules in the crystal, and that the length of the crystal edge contains $4{\cdot}64 \times 10^3$ molecules. The rate of forward propagation of the reaction is therefore $4{\cdot}64 \times 10^3$ molecules in 138 mins. or $K = 0{\cdot}56$ molecule/sec. Further, the amount of oxalate decomposed at this maximum is 2·68%. If we assume that each nucleus is responsible for the decomposition of a single layer equal to the cross section of the whole crystal, then

$$n = 0{\cdot}0268 \times 4{\cdot}64 \times 10^3 = 124 \text{ nuclei per crystal.}$$

The above value of K may now be checked by substituting for n in the expression $k = \frac{1}{2}\pi nK^2$. The average of the three relevant determinations of k_2 in Table I is $4{\cdot}7 \times 10^{-7}$, which is the rate, in fraction per sec., at $t = 600$ secs. Converting this into molecules per sec. at $t = 1$ sec., we find $\frac{1}{2}\pi nK^2 = 79$, and putting $n = 124$, we obtain $K = 0{\cdot}63$ mol./sec.

Again a value for $\frac{1}{2}\pi nK^2$ may be obtained from the vacuum decomposition by multi-

plying a (Table III) by the corresponding figure for p (Table II). Taking the data for specimen B, and converting as before to molecules per sec., we find $K = 0{\cdot}434$ mol./sec.

The agreement between these three values seems to be as good as can be expected in view of the various simplifying assumptions made.

The other constants may be obtained as follows. The value of p is $2{\cdot}83 \times 10^{-4}$. This is the number of times the plane divides per second. As the plane takes 138×60 secs. to decompose, the number of divisions per plane is 2·34. The values for this specimen at other temperatures are: 100°, 1·73; 120°, 1·91; 130°, 2·84; average, 2·21.

The value of b is $6{\cdot}12 \times 10^{-5}$. This is the number of times per second that a new plane starts from one that has already run its course. Each plane therefore gives rise to a new one every 278 mins. As this is about the time taken by vacuum decomposition to reach its maximum rate, it is clear that we were justified in ignoring Process III when considering such experiments.

The value of bnw is $1{\cdot}49 \times 10^{-7}$ (fraction per second). With our previous value of $n = 124$, tbis gives $w = 1{\cdot}96 \times 10^6$ as the number of molecules in a single plane. The number calculated from the dimensions of the crystals is $21{\cdot}5 \times 10^6$, which indicates that the size of the plane diminishes somewhat as the reaction proceeds.

The general reasonableness of these figures,* and the extent of agreement in those cases where a constant can be calculated by two entirely independent methods, indicates that the figures are of the right order of magnitude, and offers very strong support for the theory on which they are based.

SUMMARY.

The rate–time curves obtained during the decomposition of silver oxalate under various conditions have been analysed. They show that the reaction starts from a fixed number of nuclei, which depends on the history of the sample. From these it spreads in two dimensions across the planes of the crystal in the form of thin plates. These planes of reaction may branch. In a vacuum they usually do so from the leading molecule on the edge of the plane, since this possesses considerable energy from the heat of reaction. When paraffin or certain other substances are adsorbed on the surface, however, this excess energy is removed. The reaction is thereby greatly retarded, and proceeds by the spontaneous generation of fresh planes at the edges of the spent reaction planes.

Calculations show that the rate of forward propagation of the reaction is about 0·5 molecule per second at 110°, and that the energy of activation is in the neighbourhood of 32,000 cals. Various other constants have been evaluated.

I thank the Carnegie Trust for the Universities of Scotland for a Teaching Fellowship, during the tenure of which much of the work described in this and the preceding paper was done.

THE UNIVERSITY, ST. ANDREWS. [*Received, March 30th,* 1936.]

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195. *Electrolytic Dissociation Processes. Part I. The Dipole Moment of Iodine Monochloride in Solution.*

By FRED FAIRBROTHER.

Two extreme types of valency bond have been generally recognised: the homopolar or covalent bond, and the ionic bond. Further consideration has required the subdivision of these types of bond, and has postulated the existence of bonds of "mixed" type, intermediate between the two extremes. It nevertheless remains a fact that, in the pure state, most molecules are held together by bonds which are either mainly covalent or mainly ionic (compare Sidgwick, "The Co-valent Link in Chemistry," Cornell, 1933). There is, however, an important class of compounds which, although essentially covalent in the gaseous state, yet are known to undergo a transition into ionically bound molecules in suitable

* (Note added in proof). The value of b has been found to depend to some extent on the composition of the paraffin wax used. The effect is being investigated.

solvents. This transition may be partial or complete. Such transitions from a mainly covalent bond to an ionic bond in solution are of considerable importance, since they probably lie at the root of many chemical reactions. It is with such changes that this work is mainly concerned.

It has previously been shown (Fairbrother, J., 1932, **43**; 1933, **1541**; *Trans. Faraday Soc.*, 1934, **30**, 862) that the dipole moments of hydrogen chloride, bromide, and iodide are greater in solution in non-polar solvents than in the gaseous state. This effect was ascribed (*ibid.*) to an increase in the ionic character of the valency bond, brought about by the forces of solvation—a kind of incipient ionisation.

The influence of solvation in determining the type of solute bond was discussed at the same time by Rodebush (*ibid.*, p. 778), and the dissociation into free ions in solution, of an initially homopolar molecule, has been discussed in more detail by Ogg and Polanyi (*ibid.*, 1935, **31**, 604) as part of their theory of ionogenic reactions.

The present work is concerned, not only with the process of complete ionisation (as distinct from the simultaneous or subsequent electrolytic dissociation), but also with the intermediate stage between the gaseons covalent molecule and the ionically bound pair.

For hydrogen chloride dissolved in benzene the conception of an increase in the ionic nature of the valency bond is supported by the recent experiments of Plyler and Williams (*Physical Rev.*, 1936, **49**, 215), who have measured the infra-red absorption spectrum of such solutions. They find that the band, the centre of which is at 3·46μ in the gaseous hydrogen chloride, shows a slight shift to the longer wave-lengths when the substance is dissolved in benzene. This shift indicates a diminution in the vibrational frequency of the molecule, and hence a slight decrease in the binding energy between the hydrogen and chlorine nuclei. They also find that the absorption coefficient of hydrogen chloride in benzene is about 3—4 times greater than in the gaseous state, indicating that the change of electric moment in the act of absorption is greater in solution than in the gaseous state.

It may be argued that the case of the hydrogen halides, taken alone, is a special one, and not typical of such processes in general, but that it is brought about by the unique nature of the cation. For example, there is good evidence to show that the electrolytic dissociation of these compounds takes place only when the solvent molecules can enter into chemical combination with the proton (Lowry, *Chem. and Ind.*, 1923, **42**, 1048; Brønsted, *Rec. trav. chim.*, 1926, **30**, 777). It is therefore desirable to examine other cases, in which the atoms are more nearly alike in size and the electrolytic dissociation follows a more normal course. A good example of this has now been found in iodine monochloride, of which the dipole moment in solution in carbon tetrachloride and *cyclo*hexane is about twice as large as in the gaseous state. On dissolution in a polar solvent, the bond between the chlorine and iodine nuclei may become so weak that some of the molecules pass into solution as separated ions.

Experimental.

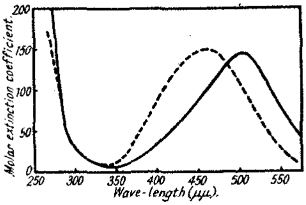
The choice of non-polar solvent in which to dissolve the iodine monochloride is very restricted owing to the great reactivity of the solute towards many organic compounds. When it dissolves in dry benzene, it does so with a hissing sound and the development of some heat. There is usually a small amount of immediate reaction, probably caused by local heating, but the subseqnent disappearance of " available halogen " (estimated with aqueous potassium iodide and sodium thiosulphate) is very slow at room temperature. Also, the reaction between dry benzene and a solution of the chloride in carbon tetrachloride is detectable only after the lapse of several hours. The solntion in benzene looks just like a solution in the tetrachloride, but a spectroscopic examination shows that the molar extinction coefficient in the visible region of the spectrum is much larger, and also that there is a large general absorption in the near ultra-violet. For these reasons, it was deemed that benzene was not a suitable solvent for the measurement of the dipole moment of iodine chloride.

Measurements were also attempted in decane (di*iso*amyl), but although the iodine chloride dissolved slowly, as would be expected from the low polarisability of the solvent, it was clear that a reaction was taking place: on standing even for a few hours, the solution became violet and a gas (probably hydrogen chloride) was evolved.

Measurements of the dipole moment were therefore made in carbon tetrachloride and *cyclo*-

hexane. Iodine chloride is probably unassociated both as a pure liquid and in solution: where cryoscopic measurements are available, they indicate a normal molecular weight in solution [compare Gmelin-Kraut, "Handb. d. anorg. Chem.," (8), 1933, Jod, p. 609 ff.]. Gillam and Morton's spectrographic measurements (*Proc. Roy. Soc.*, *A*, 1931, **132**, 152) show that iodine chloride exists in carbon tetrachloride solution as a definite undissociated compound. It also dissolves slowly and to a limited extent in *cyclo*hexane. Some spectrographic measurements of such solutions were kindly made by Mr. A. E. M. Gillam, using a Hilger E3 quartz spectrograph with a Spekker photometer; the results are in Fig. 1, together with the curve (broken line) obtained by Gillam and Morton for carbon tetrachloride solutions. They show that the molar extinction coefficient of 145 in *cyclo*hexane solution is in excellent agreement with that of 150 in carbon tetrachloride. The absorption maximum, however, is at about 505 μμ whereas in carbon tetrachloride solutions it is at 460 μμ. On standing at room temperature, iodine chloride slowly reacts with *cyclo*hexane. This is most noticeable in very dilute solutions, which gradually acquire a violet tinge after a few days. The reaction, however, is very slow, and does not affect the results given below.

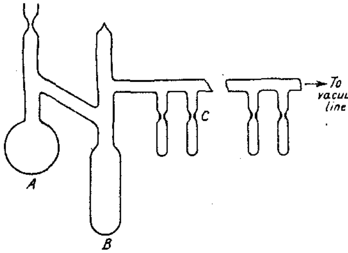
FIG. 1.



The carbon tetrachloride (Kahlbaum) was freed from residual traces of sulphur compounds by repeated treatment with alcoholic potash (Schmitz-Dumont, *Chem.-Ztg.*, 1897, **21**, 510). The *cyclo*hexane, a commercial product, was shaken with 100% sulphuric acid to remove benzene, and then fractionated several times: spectrographic examination showed that it was free from benzene. Both solvents were kept in contact with phosphoric oxide for several weeks prior to the final distillation.

Since iodine monochloride reacts instantly with water and fumes when exposed to the air, it was necessary to minimise the latter exposure; the chloride was therefore manipulated in the following manner. The commercial substance was first fractionally frozen several times: Stortenbeker (*Rec. trav. chim.*, 1888, **7**, 152) recommended this method of purification in preference to fractional distillation on account of dissociation, which occurs more readily when the substance is not dry (Curtis and Patkowski, *Phil. Trans.*, 1934, **232**, *A*, 395). The monochloride was then melted, kept in contact with phosphoric oxide at 30° for several days, and decanted into the flask *A* (Fig. 2), which was then sealed off. The pressure in the system was reduced, and the iodine chloride subjected to a rough fractionation at room temperature, the first fraction passing through the apparatus to a liquid-air trap, the middle fraction being condensed on fresh phosphoric oxide in *B*, which was cooled in solid carbon dioxide-acetone, and the remainder left in *A*; *A* was then sealed off from *B*. The pressure in the system was now further reduced, and the chloride fractionally sublimed from the phosphoric oxide in *B* into the little side tubes. During this process, *B* was kept at 0° or slightly above, and the side tube in liquid air. The pressure of permanent gas in the system during this sublimation was never greater than 10^{-4} mm., and for most of the time was below 10^{-6} mm.: iodine chloride possesses sufficient vapour pressure for a fairly rapid sublimation under these conditions. During this process much of it passed through the apparatus and was caught by the liquid-air traps. When sufficient had been condensed in one of the little tubes, it was sealed off in a vacuum, the glass having been thickened at *C* for this purpose. Owing to the absence of air in the tubes, the monochloride readily sublimed from one part of the tube to another and formed magnificent crystals on standing. It was then condensed, by cooling in solid carbon dioxide, to one end of the tube, where it remained when the tube

FIG. 2.



was allowed to regain room temperature. A scratch was made near the empty end of the tube, and the latter and its contents weighed. The tube was then cracked by a hot rod, the pieces separated, and the monochloride quickly slipped into a weighed quantity of solvent contained in a 100-c.c. stoppered flask. In this way contact with the air was reduced to a minimum. The tube was usually broken cleanly into two pieces, which were subsequently washed and dried, and the weight of chloride was obtained by difference with due allowance for vacuum corrections.

The dielectric constants were measured in a platinum plate condenser, of about 215 μμF capacity when filled with dry air, by a resonance method which was essentially as previously described (*Proc. Roy. Soc.*, *A*, 1933, **142**, 173). The chief modifications to this method were the use of a frequency of 200 kc. instead of 1000 kc., in order to decrease the inductance corrections, and the use of a steady current to balance part of the rectified resonance current so as to use a higher portion of the resonance curve and a more sensitive galvanometer. The standard variable condenser was a Muirhead Type II condenser of 1250 μμF maximum capacity, with quartz insulation. The frequency of 200 kc. was obtained by a Dynatron oscillator with a buffer-amplifier valve between the Dynatron valve and the coupling to the resonance circuit. The power factors of the solutions (as shown by the shape of the resonance curve) were not detectably different from those of the pure solvents, which indicated the absence of free ions.

The densities were measured in a capped glass pyknometer of the Sprengel type. The mol.-fractions of solute f_2, dielectric constants ϵ, densities d, and polarisations are given in the table.

Iodine in carbon tetrachloride.

f_2.	ϵ.	d.	P_{12} (c.c.).	P_2 (c.c.).
0·000	2·236	1·5939	28·16	—
0·007366	2·261	1·5998	28·47	69·9
0·01028	2·270	1·6021	28·57	68·4
0·01684	2·292	1·6068	28·85	68·9
0·03036	2·336	1·6184	29·34	66·9
0·05559	2·402	1·6304	30·14	63·8

$_\infty P_2 = 71$ c.c.

Iodine chloride in cyclo*hexane.*

f_2.	ϵ.	d.	P_{12} (c.c.).	P_2 (c.c.).
0·000	2·021	0·7786	27·42	—
0·01126	2·049	0·7909	27·84	63·9
0·01397	2·0555	0·7940	27·92	63·1
0·01601	2·059	0·7959	27·98	62·0
0·01787	2·064	0·7982	28·04	62·0

$_\infty P_2 = 69·5$ c.c.

Discussion.

The absorption band-spectrum of the vapour of iodine chloride has been much studied (for references, see Jevons, "Report on the Band-spectra of Diatomic Molecules," Cambridge, 1932). In the ground state it is a $^1\Sigma$ molecule, with a valency bond that is essentially homopolar or covalent. The dielectric polarisation of the gaseous substance at 61·1—161·1° has been measured by Luft (*Z. Physik*, 1933, **84**, 767), whose results may be expressed in the form $P = 31 + 1700/T$ c.c., indicating a dipole moment of 0·5 D. This corresponds to a total molar polarisation of 37 c.c. as compared with the present value of about 70 c.c. in solution. It is clear, therefore, that a considerable increase in the dipole moment of iodine chloride occurs when it is dissolved in carbon tetrachloride or *cyclo*hexane.

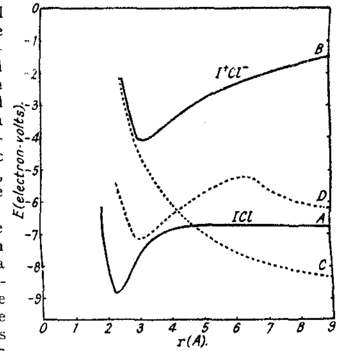
Some measurements of the polarisation of iodine chloride in carbon tetrachloride solution have also been made by Malone and Ferguson (*J. Chem. Physics*, 1934, **2**, 99), who found $_\infty P_2 = 60$ c.c. which is less than the present values. They state that their solutions tarnished the gold plating of the cell. In the present work there was no detectable action whatever on the platinum plates of the cell, which remained bright throughout the measurements. Their results, however, agree with the author's in that the polarisation in carbon tetrachloride is considerably greater than that in the gaseous state.

There do not appear to be any recorded measurements of the refractive index of iodine chloride, either in the pure state or in solution. Moreover, the calculation of the electronic polarisation from refractive-index measurements in the visible region of the spectrum is uncertain on account of the strong absorption bands in the spectrum. We may, however, obtain a rough estimate of P_E for the homopolar molecule from the mean of the molar refractivities of gaseous iodine and chlorine. From Cuthbertson's figures for these (*Phil. Trans.*, 1914, *A*, **213**, 1) at 6708 A., the molar volume being taken as 22·4 l., this mean is 20·5 c.c. The sum of the refractivities of the separated ions will be slightly less than the sum of the refractivities of Cl' and atomic iodine. Fajans and Joos (*Z. Physik*, **1924**, **23**, 1) give the former as 9 c.c., and half the refractivity of molecular iodine, calculated from Cuthbertson's data (*loc. cit.*) at 6708 A., is 14·7 c.c.: the sum is 23·7 c.c. We may reason-

ably assume, therefore, an upper limit of 24 c.c. for P_{E+A}, whence it seems that Luft's value of 31 c.c., obtained by extrapolation, is too high and may arise from the well-known experience that small individual errors in such measurements are greatly magnified when the polarisation is extrapolated to $1/T = 0$. His total molar polarisation figures at 60° and a value of 24 c.c. for P_{E+A} indicate a moment of 0·8 D. In the same way the present results show, for solution in carbon tetrachloride, $\mu = 1{\cdot}49$ D, and in *cyclo*hexane $\mu = 1{\cdot}47$ D.

It is suggested that this increase in dipole moment is caused by an increase in the ionic character of the valency bond. It is probably accompanied by a slight increase in the nuclear separation. Pauling and Yost (*Proc. Nat. Acad. Sci.*, 1932, **18**, 414) and Pauling (*J. Amer. Chem. Soc.*, 1932, **54**, 3570) have pointed out that the actual bond energy of pure iodine chloride, *viz.*, 2·143 e.v., is 0·142 e.v. higher than the mean of the bond energies of iodine and chlorine, which indicates that the wave function representing the bond may contain ionic terms, even when we are dealing with the gaseous state.

Fig. 3.



The polarising influence of solvation will then increase the relative probability of the configuration I^+Cl^-, this probability increasing as the polarisability of the solvent (and hence the solvation energy) increases. In solvents such as carbon tetrachloride and *cyclo*hexane, we are concerned only with a partial "ionisation." As the dielectric constant of the solvent increases, the ionic character of the bond becomes more marked, until the ionic terms greatly exceed the covalent terms.

Some idea of the energy necessary for the various steps in the electrolytic dissociation of iodine chloride may be gained from a consideration of the approximate potential-energy curves relating to the respective states. These are given in Fig. 3. The curve *A* for the gaseous molecule, which is essentially a homopolar molecule, has been calculated by the well-known Morse expression (*Physical Rev.*, 1929, **34**, 37), *viz.*, $E = D[2e^{-a(r-r_0)} - e^{-2a(r-r_0)}]$ by using the following data (Jevons, *loc. cit.*): $D = 2{\cdot}143$ e.v., $\omega_e = 384{\cdot}6$ cm.$^{-1}$, $r_e = 2{\cdot}310$ A., $\alpha = 1{\cdot}875$. The effect of the solvent atmosphere on this curve is small, so that it can be taken to refer to the homopolar molecule either in the gaseous state or in solution.

The curve *B*, which represents the potential energy of the unsolvated ions I^+ and Cl^- as a function of nuclear separation, has been calculated by the expression $E = -e^2/r + b/r^9$. The value of the coefficient *b* is obtained by equating the first derivative to zero and putting *r* equal to the equilibrium distance in the lowest state. For this purpose, and for the subsequent estimation of the solvation energies, it is necessary to assign an ionic radius to the positive iodine ion. This can only be done indirectly, for no direct evidence is available. There seems no doubt, however, that iodine can exist separately as a positive ion: *e.g.*, it forms a number of other stable compounds with electronegative atoms and radicals (compare Gmelin-Kraut, *op. cit.*, p. 454). From a consideration of the radii of the isoelectronic tellurium atom, the neutral iodine atom, and of a number of other atoms and ions down to I^{+5} and I^{+7} (Smithsonian Physical Tables, 1934, 491), all of which lie near a straight line when plotted against the effective atomic number (the total number of extra-nuclear electrons), it appears that a very probable radius for I^+ is 1·30 A. The radius of Cl^- is taken as 1·81 A. (Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 765), and the equilibrium nuclear separation of the ion pair as the sum of these, *viz.*, 3·11 A. In this, no account has been taken of the compressibilities of the ions, which will affect both the equilibrium separation and the shape of the left-hand branch of the curve: but this will not affect the present argument.

The ionisation potential of iodine I $\longrightarrow$ $I^+ + e$ is 10·44 e.v. (Evans, *Proc. Roy. Soc.*, *A*, **1931**, **133**, 417), and the electron affinity of chlorine is 3·75 e.v. The asymptotic value of the potential energy of the separated ions must therefore lie 10·44 − 3·75 = 6·69 e.v. above the asymptote of the homopolar curve.

If the ions be solvated, their potential energies will be reduced accordingly, and therefore the potential-energy curve relating to the solvated ions will lie below *B*. When the solvent is such that actual dissociation of the homopolar molecule occurs, the form of the curve will be as shown at *C*, the position depending both on the solvation energy and on the size of the solvent molecules.

The change in potential energy when an ion of radius a and charge e is immersed in a homogeneous medium of dielectric constant ϵ is given by $-\Delta E = e^2(1 - 1/\epsilon)/2a$. The actual energy of solvation of an ion will generally be somewhat less than this, since, first, the medium surrounding the ion is not homogeneous but consists of discrete solvent molecules, and secondly, the use of the macroscopic dielectric constant is not strictly justifiable since it is measured at low field strengths whereas the field strength in the neighbourhood of an ion may be very large. For example, the decrease in potential energy of a chlorine ion of radius 1·81 A., when immersed in a homogeneous medium of $\epsilon = 81$, as calculated by the above expression is 3·9 e.v.; on the other hand, Webb (*J. Amer. Chem. Soc.*, 1926, **48**, 2589) has calculated the free energy of hydration of the chlorine ion to be 70·1 kg.-cals. = 3·16 e.v.

Nevertheless, we may use this expression to calculate to a first approximation the energy of solvation of the ions with which we are concerned. Such a calculation shows that the total energy of solvation of I^+ ($a = 1·30$ A.) and Cl^- ($a = 1·81$ A.), when completely separated from one another and immersed in a medium of $\epsilon = 2$, is 4·7 e.v. The energy of solvation of the ion-pair in contact will be less than this, of the order of 75%, since the ions will be surrounded by fewer solvent molecules. The potential-energy curve of the ion-pair in a medium of low dielectric constant, though it cannot be completely represented on a two-dimensional diagram, will be somewhat of the form shown at *D* (Fig. 3).

It is clear, therefore, that the solvation energy is sufficient to permit of a greatly increased interaction between the covalent and the ionic state of iodine chloride when dissolved in a medium, even of low dielectric constant.

A closer approximation to the actual energy of solvation may perhaps be made in the case of small solvent molecules, by assuming, say, a four-fold co-ordination of solvent molecules around the ion and calculating the energy of interaction between the ion and the solvent molecule by the expression $E = \alpha e^2/2r^4$, in which α is the polarisability of the solvent molecule and r is the distance between its centre and the ion nucleus. For large solvent molecules this becomes less approximate as the binding force is mainly exerted between the ion and the atoms of the solvent molecule which are closest to it; moreover, in this we must again calculate α from macroscopic measurements. It may be added also that, when dealing with *polar* solvents, we must include in the polarisability which is effective in solvation, not only the optical or electron polarisability, but also the orientation polarisability arising from the dipole moment of the solvent; otherwise, the ionising power of solvents would not run parallel with the dielectric constant.

In the case of iodine chloride, a total ionic solvation energy of 7 e.v., corresponding to immersion in a medium of $\epsilon = 3·9$, would bring the potential-energy curve of the solvated ions at infinite separation below that of the homopolar molecule, which it would then cross at a moderate separation. The ionic curve would then be almost wholly repulsive, and we should expect electrolytic dissociation to occur. This, in fact, is what happens. Preliminary measurements made at 20° show that iodine chloride dissolved in chlorobenzene ($\epsilon = 5·8$) is an extremely weak electrolyte, but conducts sufficiently well to preclude the measurement of its dielectric constant by a resonance method. In ethylene dichloride ($\epsilon = 10$) it conducts very much better, but is still a very weak electrolyte. Walden (*Z. physikal. Chem.*, 1903, **43**, 385) has measured its conductivity in arsenic trichloride, sulphuryl chloride, and liquid sulphur dioxide, and Solly (*Phil. Mag.*, 1836, **8**, 400) observed that the liquid substance itself conducted electricity.

Although, in the above, the electrolytic dissociation has been discussed on the basis of

curves *A* and *C* (Fig. 3), the homopolar curve *A* being taken as relating to the initial state of the system in solution, it should be remarked that this is not strictly so in fact, since the dissolution of iodine chloride in the solvent is accompanied by an increase in the dipole moment. Hence it follows that the lowest state of the molecule in the undissociated form will be one which is lower than *A* by reason of the ionic terms introduced into the bond energy.

Whether or not any given molecule will undergo an increase of dipole moment as compared with the gaseous state, on dissolution in a non-polar solvent, and electrolytic dissociation in a suitably polar solvent, appears to depend chiefly on two factors, providing that the solvent molecules do not enter into chemical combination with part of the solute molecule to form another kind of ion, *viz.*, (*a*) on the solvation energy available, which in turn depends on the ionic radii and the polarisability of the solvent molecules, and (*b*) on the energy difference between the wholly ionic and the wholly covalent state, *i.e.*, on the difference between the energy required to remove an electron from the positive radical and the electron affinity of the negative radical.

SUMMARY.

The dipole moment of iodine monochloride has been measured in solution in carbon tetrachloride and in *cyclo*hexane, and in these solutions it is about twice as large as in the gaseous state. The results are interpreted as being due to an increase in the ionic character of the valency bond of the substance. The approximate potential-energy curves of the homopolar and the ionic state have been calculated, and also the approximate energy of solvation of the ions. It is shown that the latter is sufficient to account for the observed results. The results are also discussed in relation to the process of electrolytic dissociation into free ions, of an initially covalent molecule. Preliminary results are mentioned to confirm the conclusion that, in a medium of dielectric constant slightly higher than those of the solvents used, the iodine chloride would give rise to free ions.

I wish to thank my colleague, Mr. M. G. Evans, for helpful discussions, and the Royal Society and Messrs. Imperial Chemical Industries, Ltd., for grants for the purchase of apparatus.

THE UNIVERSITY, MANCHESTER. [*Received, March 17th, 1936.*]

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196. *The Rotatory Dispersion and Circular Dichroism of 2 : 2-Dinitrocamphane in the Ultra-violet.*

By STOTHERD MITCHELL and ROY R. GORDON.

OPTICALLY active organic substances containing the groups CO, CS, Ph, Cl, Br, I, N_3, ONO, and NO have been used by a number of observers for studying rotatory dispersion and circular dichroism (see Mitchell, " The Cotton Effect," London, 1933). We have now employed a compound containing the nitro-group. We bad intended to use camphor-ψ-nitrol, but as it was too unstable for polarimetric work we examined its oxidation product, 2 : 2-*dinitrocamphane.*

Rotatory dispersion data for solutions of this substance in alcohol are given in Table I, and specific rotation, $[\alpha]$, is plotted against wave-length, λ, in the figure (curve 1, full line). The rotation falls to a negative maximum at about 3020 A., and thereafter increases, passing through zero at 2762 A. It was not found practicable to follow the curve further into the ultra-violet than 2666 A., owing to the strong absorption beyond this limit.

The absorption was examined with a Hilger sector spectrophotometer, a 2-cm. column of an alcoholic solution containing 0·0390 g./100 c.c. being used. In curve 2 (full line) the molecular extinction coefficient, ε, is plotted against wave-length, and the result is similar to that recorded for several aliphatic compounds containing the nitro-group (cf. Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 504; Zelinsky and Rosanoff, *Z. physikal. Chem.*, 1912, **78**, 639).

Table II contains the circular dichroism data, alcohol being again used as solvent. The

TABLE I.

Solutions : (*a*) 0·1563, (*b*) 0·6250, (*c*) 0·3125 g./100 c.c.; l = 0·99 cm.; t = 17°.

Soln.	λ.	α.	[α].	Soln.	λ.	α.	[α].
(*a*)	2980	−0·40°	−2586°	(*b*)	3720	−0·50°	− 808°
	2946	−0·35	−2262		3558	−0·60	− 970
	2912	−0·25	−1615		3350	−0·70	−1132
	2869	−0·20	−1293		3248	−0·80	−1293
	2833	−0·15	− 970		3222	−0·90	−1454
	2804	−0·10	− 647				
	2762	0·00	0				
	2706	+0·10	+ 647	(*c*)	3193	−0·50	−1616
	2689	+0·15	+ 970		3126	−0·70	−2262
	2666	+0·20	+1293		3047	−0·80	−2586

TABLE II.

Concn. = 0·1563 g./100 c.c.; l = 0·99 cm.; t = 17°.

λ.	Ellipticity.	$\epsilon_l - \epsilon_r$.	ε.	$(\epsilon_l - \epsilon_r)/\epsilon$.	λ.	Ellipticity.	$\epsilon_l - \epsilon_r$.	ε.	$(\epsilon_l - \epsilon_r)/\epsilon$.
3030	−0·20°	−0·90	101	−0·009	2778	−0·75°	−3·35	283	−0·012
3009	−0·30	−1·34	113	−0·012	2739	−0·75	−3·35	293	−0·011
2972	−0·35	−1·56	138	−0·011	2666	−0·65	−2·91	308	−0·009
2957	−0·40	−1·79	152	−0·012	2644	−0·55	−2·46	311	−0·008
2946	−0·45	−2·01	162	−0·012	2620	−0·50	−2·24	315	−0·007
2920	−0·50	−2·24	189	−0·012	2580	−0·40	−1·79	323	−0·006
2900	−0·55	−2·46	210	−0·012	2550	−0·35	−1·56	338	−0·005
2885	−0·65	−2·91	227	−0·013					

molecular ellipticity (col. 3) is given by $\varepsilon_l - \varepsilon_r = (4\tau \times 0{\cdot}4343)/lc$, where τ is the observed ellipticity expressed in radians, l the length of tube in cm., and c the concentration in g.-mols./litre. When the molecular ellipticity is plotted against wave-length, a symmetrical curve is obtained (curve 3, full line) which has a negative maximum at 2770 A., very close to where the rotation curve crosses the axis. Values of ε shown in col. 4 of Table II were read off from the absorption curve for the required wave-lengths. The last column contains the dissymmetry factor $(\varepsilon_l - \varepsilon_r)/\varepsilon$, which is fairly constant down to 2778 A., after which it decreases.

This constancy of the dissymmetry factor over the long-wave portion of the absorption band suggests that the selective absorption due to the nitro-groups covers the same wave-length range as the ellipticity. Furthermore, the form of the rotatory dispersion curve indicates that it is controlled to a great extent by the same absorption band. It is possible to test these assumptions in the following manner.

The molecular ellipticity may be expressed by the equation

$$(\varepsilon_l - \varepsilon_r) = (\varepsilon_l - \varepsilon_r)_{\max.} e^{-[(\lambda - \lambda_0)/\theta]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which is essentially that used by Kuhn and Szabo (*Z. physikal. Chem.*, 1931, *B*, **15**, 63) but with wave-lengths substituted for freqnencies. In this equation, the parameter θ is defined by $\lambda' = 1{\cdot}6651\theta$, where λ' is the half-width of the band. The values $(\varepsilon_l - \varepsilon_r)_{\max.}$ = − 3·37, λ' = 400 A., and λ_0 = 2770 A. are read from the full-line curve 3, and equation (1) then gives the broken curve 3.

The form of the rotatory absorption band may now be calculated from the parameters λ_0 and θ, obtained from the curve of circular dichroism, using the equation

$$\varepsilon = \varepsilon_{\max.} e^{-[(\lambda - \lambda_0)/\theta]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(cf. Kuhn and Braun, *Z. physikal. Chem.*, 1930, *B*, **8**, 281; Lowry and Hudson, *Phil. Trans.* 1933, *A*, **232**, 117).

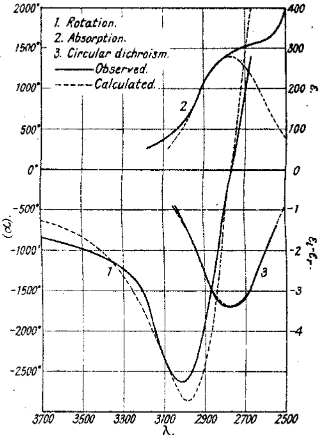
Since the dissymmetry factor remains constant at 0·012 over the long-wave side of the absorption band (Table II), it follows that $\varepsilon_{\max.}$ must have a value very near to 3·37/0·012 = 280, and the broken curve 2 can now be calculated.

Finally, an approximate calculation of the contribution of the nitro-groups to the rotatory dispersion of the molecule may be made by means of equation (3), which is a mod

fication by Lowry and Hudson (*loc. cit.*) of an equation formulated by Kuhn and Braun (*loc. cit.*) :

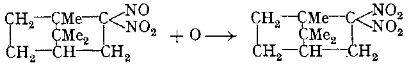
$$[\alpha] = \frac{[\phi]\lambda_\phi}{m\ \lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta} e^{x^2}\,dx + \frac{\theta}{2(\lambda+\lambda_0)}\right] \quad . \quad . \quad . \quad . \quad (3)$$

where $[\phi]$ = maximum value of $[\alpha]$ which occurs at wave-length λ_ϕ, m = maximum value of the terms within the large brackets, λ_0 and θ have values as above, and the other symbols have their usual significance. The result is shown as the broken curve 1, and it is clear from the figure that the difference curve (not shown) obtained from this and the full-line curve 1 must cross the axis of zero rotation at several points, so that it is not possible to decide whether the residual rotation should be regarded as positive or negative. The ripples in the residual curve are probably due partly to experimental error and partly to the approximate nature of equation (3). Similar results have been obtained by Hudson, Wolfrom, and Lowry (J., 1933, 1189) with tetra-acetyl μ-arabinose, and by Baldwin, Wolfrom, and Lowry (J., 1935, 700) with penta-acetyl μ-fructose. In the present case it would appear that the contribution of the nitro-groups accounts for essentially the whole of the observed rotation.



Experimental.

Preparation of 2 : 2-*Dinitrocamphane*.—Charlton, Earl, Kenner, and Luciano (J., 1932, 37) observed that when camphor-ψ-nitrol was freshly prepared it melted at 60°, but on standing over-night the m. p. fell to 52°. We found that the blue nitrol readily absorbs oxygen and loses its colour. By exposing a quantity of the nitrol to the air on a porous plate, a camphor-like product was obtained which, after being crystallised several times from aqueous alcohol, had m. p. 107·5—108·5° (Found : C, 53·0; H, 7·0; N, 12·5. $C_{10}H_{16}N_2O_4$ requires C, 52·6; H, 7·0; N, 12·3%), and was concluded to be 2 : 2-*dinitrocamphane* :



Apparatus.—For measuring the rotations, an ultra-violet polarimeter of the type described by Kuhn (*Ber.*, 1929, **62**, 1727) was constructed. The optical parts and graduated circles were obtained from Messrs. Adam Hilger, Ltd., the castings for the iron bed and standards were made from patterns prepared in our workshop, and the instrument was assembled by Mr. Robert McCulloch.

A simple Rochon prism of left-handed quartz, 4 cm. long and 2 × 2 cm. aperture, served as analyser. The polariser was made from a right-handed quartz prism of the same dimensions and had a fixed half-shadow angle of 5°. Both polariser and analyser were provided with a graduated circle, and each was mounted as a separate unit which could be moved as required on the slides of the iron bed. The condensing lens fitted in front of the polariser was a plano-convex quartz lens of 5″ focal length, and the projection lens fitted behind the analyser was an achromatic quartz fluorite doublet of focal length 8·27″. As light source we used an iron arc with a current of 3 amps., the coil of an electromagnet being inserted in the circuit to steady the arc as recommended by Houstoun (" Treatise on Light," London, 1930, p. 250). The arc was focused on a small circular hole in a metal screen by means of a plano-convex quartz lens of 1·5″ focal

length. End pieces for the observation tube were made from selected pieces of fused silica, free from strain, supplied by The Thermal Syndicate, Ltd.

The polarimeter was used in conjunction with a Hilger medium quartz spectrograph. Only the ordinary rays from the polariser were allowed to enter the observation tube (cf. Lowry and Gore, *Proc. Roy. Soc.*, 1932, *A*, **135**, 13), and only the ordinary rays from the analyser were permitted to pass into the spectrograph, the dividing line of the polariser being focused with the projection lens across the centre of the slit and the height of the slit being adjusted to 4 mm. by means of a V-shaped slide. After the zero had been determined, a series of photographs was taken for different positions of the analyser, and the wave-lengths were found for which the contiguous parts of each photograph had equal intensity. Ilford Iso-Zenith plates (H and D 650) were used throughout, and the exposnres were varied from 2 to 40 minutes, depending on the amount of absorption of the light at the point of interest on the plate.

For measuring the ellipticities, we used the method of Kuhn and Braun (*Z. physikal. Chem.*, 1930, *B*, **8**, 445), in which a Fresnel rhomb was placed between the polariser and the observation tube. Different settings were given to the polariser, and the wave-lengths for which these gave equal intensity were found from a photographic plate in the same way as for the rotations. Kuhn and Braun constrncted a rhomb suitable for use in the ultra-violet by fitting a brass case of the required shape with windows of fused silica and then filling it with water, but as fused silica of optical quality is now available (cf. Lowry and French, J., 1932, 2654), our rhomb was made of this material; it had an aperture 1·7 × 1·7 cm., and an angle of 51° 47′ which was calculated from Fresnel's eqnation (*Ann. Chim. Phys.*, 1831, **46**, 256) by using the value $n_{2743} = 1{\cdot}4964$ for fused silica. The rhomb was inserted after the polariser, and optical alinement was then restored by raising the optical train from the rhomb to the light source. To facilitate this, the tubular bearing for the graduated circle of the polariser passed through a block which could be raised between vertical guides by means of a screw, the rhomb holder being slid into grooves at the back of the block.

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UNIVERSITY OF GLASGOW. [*Received, March 30th*, 1936.]

197. *Ethyl Esters of β-Arylaminocrotonic Acids.*

By S. COFFEY, J. K. THOMSON, and F. J. WILSON.

THE following types of compound can be obtained directly from ethyl acetoacetate and a primary arylamine according to the experimental conditions: (1) esters of β-arylaminocrotonic acids, CMe(NHR)⁚CH·CO_2Et, (2) arylamides of acetoacetic acid, Me·CO·CH_2·CO·NHR, (3) arylamides of β-arylaminocrotonic acids, CMe(NHR)⁚CH·CO·NHR, (4) *s.*-diarylureas, $CO(NHR)_2$, (5) derivatives of 2-hydroxylepidine.

A considerable number of ethyl esters of β-arylaminocrotonic acids have been prepared by various investigators by the reaction Me·CO·CH_2·CO_2Et + R·NH_2 = Me·C(NHR)⁚CH·CO_2Et + H_2O. Varied conditions are described for the preparation and in many instances different products are obtained on repetition. Knorr (*Ber.*, 1883, **16**, 2593) obtained ethyl β-anilinocrotonate by reaction at the ordinary temperature, Conrad and Limpach (*ibid.*, 1887, **20**, 944; 1888, **21**, 523, 1649; 1891, **24**, 2990) prepared a number of such esters by the same method but preferred to carry out the reaction on the water-bath, as the separation of water is accelerated thereby. Gibson, Harihan, Menon, and Simonsen (J., 1926, 2247), however, on attempting to prepare ethyl β-1-naphthylaminocrotonate by Conrad and Limpach's method obtained instead acetoaceto-1-naphthalide, as would be expected from our results; the reaction went, however, in the desired direction in the cold in the presence of a few drops of diethylamine as catalyst. Nair and Simonsen (*ibid.*, p. 3140) used piperidine as catalyst. In a patented method, Limpach (*Ber.*, 1931, **64**, 969) prepared ethyl β-anilino-, -*p*-phenetidino-, and -1-naphthylaminocrotonates at the ordinary temperature. Many of these esters have not been definitely characterised or analysed. Pellizzari (*Gazzetta*, 1891, **21**, 340), in preparing ethyl β-*m*-carb-

oxyanilinocrotonate, used boiling alcohol as solvent. According to I.G. patents (F.P., 1930, 680, 384, Hung. P., 1930, 101, 504) ethyl β-dehydrothiotoluidinocrotonate is prepared by heating the reactants on the water-bath for 10 hours. Jadhav (*J. Indian Chem. Soc.*, 1930, **7**, 669) prepared ethyl β-*p*-phenetidino-, and -*p*-chloroanilino-crotonates by reaction at the ordinary temperature and claimed to have obtained ethyl β-*p*-nitroanilinocrotonate by refluxing ethyl acetoacetate with *p*-nitroaniline. We could not confirm the latter observation, the only reference in the literature to a β-nitroarylaminocrotonic ester, and we regard his product as acetoaceto-*p*-nitroanilide. Other ethyl β-arylaminocrotonates described in the literature are usually prepared at the ordinary temperature; in many instances it is recorded that warming on the water-bath accelerates the reaction.

It is therefore not obvious what conditions facilitate the reaction. One of us found that, although commercial ethyl acetoacetate reacted with aniline in the cold in the course of a few days as described by Knorr, no reaction occurred for a prolonged period, often 20 days, if carefully purified ester was used. It was discovered that the Knorr reaction could be accelerated by the addition of acid catalysts; thus a mixture of ester and aniline which remained unchanged for nearly a month gave ethyl β-anilinocrotonate in 5 minutes on addition of a small quantity of aniline hydrochloride, heat being evolved; the speed of the reaction was roughly proportional to the strength of the acid. Alkalis (sodium hydroxide, sodium carbonate, ammonia, borax, piperidine) had only a slight catalytic effect; solvents had little if any effect. It appeared that the reaction was very sensitive to acids, but was not inhibited by alkalis.

Further work on the influence of catalysts on the general reaction has confirmed these conclusions. We prepared the following esters by Knorr's method (ordinary temperature, no catalyst), using carefully purified ethyl acetoacetate: ethyl β-anilino-, -*p*-anisidino-, -*p*-phenetidino-, -*m*-4-xylidino-, -p-*xylidino-*, -*p*-chloroanilino-, -p-*phenylamino-anilino*-crotonates; the rate of reaction, as judged by the separation of water, varied from a few hours to many days. These esters, and ethyl β-o-*chloroanilino-* and -m-*chloro-anilino-crotonates*, were also prepared under the same conditions as before, but with addition of a very small quantity of the corresponding arylamine hydrochloride or iodine; the reaction was so much accelerated that water commenced to separate in a few minutes. The β-*o*- and -*m*-chloroanilinocrotonic esters have not yet been obtained without the use of a catalyst. In a number of instances traces of alkalis (sodium hydroxide, ammonia, pyridine, diethylamine, etc.) were tried, but in general they did not accelerate or inhibit the reaction. All attempts to prepare ethyl β-arylaminocrotonates from *o*-, *m*-, and *p*-nitroanilines, *m*-nitro-*p*-toluidine, *p*-chloro-*o*-nitroaniline, and 2 : 4-dinitroaniline failed; the addition of ether, alcohol or in some instances excess of ester did not have any effect even on gentle warming and in presence of acid or iodine as catalyst.

It was thought that β-arylaminocrotonoarylamides, for which two of us (Thomson and Wilson, J., 1935, 111) had already worked out general methods of preparation, might be obtained from ethyl β-arylaminocrotonates by heating with arylamine, $Me{\cdot}C(NHR){:}CH{\cdot}CO_2Et + R{\cdot}NH_2 = Me{\cdot}C(NHR){:}CH{\cdot}CO{\cdot}NHR + EtOH$. The experiment was carried out by heating equivalent amounts of the reactants for about 5 hours in a solvent of suitable boiling point snch as petroleum (b. p. above 120°) or chlorobenzene. In only two instances were small quantities of the desired products, β-*p*-xylidinocrotono-*p*-xylidide and β-*o*-chloroanilinocrotono-*o*-chloroanilide, obtained, the latter compound once only. It is concluded that in the preparation of β-arylaminocrotonoarylamides these esters are not intermediate compounds.

Experimental.

The ethyl acetoacetate was purified by keeping over-night with anhydrous sodium carbonate and after filtration was fractionally distilled at a pressure of not more than 6 mm.; the refractive index always corresponded within the limits of experimental error with the values given by Meyer and Schoeller (*Ber.*, 1920, **53**, 1410).

Ethyl β-anilinocrotonate was prepared by mixing equimolecular quantities of aniline (18·6 g.) and ethyl acetoacetate (26 g.) with addition of approximately 0·05 g. of aniline hydrochloride; in about 6 minutes water began to separate and the temperature rose slightly.

After 12 hours, the water was removed by centrifuging and absorption by filter-paper; the pale greenish-yellow oil, after being dried with sodium sulphate, distilled almost wholly at 135—139°/6—7 mm. except for a little unchanged ester and aniline and a very small residue. On redistillation it had b. p. 137—139°/6 mm. (Décombe, *Ann. Chim.*, 1932, **18**, 118, gives 142—145°/5 mm.) (Found: C, 70·3; H, 7·6; N, 6·8. Calc.: C, 70·2; H, 7·4; N, 6·8%). Iodine as a catalyst is as efficient as aniline hydrochloride, and one drop of hydrochloric acid caused the appearance of water in about 1 minute.

Ethyl β-*p*-anisidinocrotonate (Conrad and Limpach, *Ber.*, 1888, **21**, 1649) was prepared by gently warming a mixture of equimolecular quantities of ethyl acetoacetate (6·5 g.) and *p*-anisidine (6·15 g.) until the latter had dissolved, removing it from the water-bath, adding a trace of catalyst, and then shaking thoroughly. In these experiments the amount of solid catalyst was about 0·01—0·02 g., the amount of liquid catalyst was a small drop from the end of a capillary tube. The times which elapsed before the appearance of water were: (1) with no catalyst, about 1 hour; (2) iodine, about 1½ minutes; (3) hydrochloric acid, ½ minute; (4) pyridine, about 1 hour. The combined products after removal of water in an evacuated desiccator and recrystallisation from *iso*propyl ether gave prisms, m. p. 45—45·5° (Found: N, 6·1. Calc.: N, 6·0%); yield, about 90%.

Ethyl β-*p*-phenetidinocrotonate is first referred to by Riedel (D.R.-P. 76798; Frdl., **4**, 1199), who gave m. p. 52·5—53°. It was prepared but not purified by Limpach (*loc. cit.*) and was later described by Jadhav (*loc. cit.*) as melting at 60—61°. To a mixture of equimolecular quantities of ethyl acetoacetate (6·5 g.) and *p*-phenetidine (6·85 g.), a catalyst was added. The times which elapsed before turbidity appeared were: (1) with no catalyst, over-night; (2) *p*-phenetidine hydrochloride, 14—20 minutes; (3) iodine, 4—12 minutes; (4) diethylamine, no reaction over-night, but on keeping in a vacuum crystals of the substance appeared after several days. The products from (1), (2), and (3) solidified over-night; the crystals after drying on porous tile and recrystallisation from dilute alcohol or *iso*propyl ether melted at 54—54·5°; yield, 85% (Found: C, 67·4; H, 7·5; N, 5·7. Calc.: C, 67·5; H, 7·6; N, 5·6%).

Ethyl β-o-*chloroanilinocrotonate* was prepared from ethyl acetoacetate and *o*-chloroaniline with addition of a trace of *o*-chloroaniline hydrochloride; in about 20 minutes water commenced to separate: without a catalyst, there was no apparent reaction after 1 week. After removal of the water in an evacuated desiccator the product was distilled at 2—3 mm.; about 25% (unaltered reactants) distilled below 80°; the remainder, consisting of the desired substance, passed over at 141—143°/2 mm., leaving a negligible residue (Found: N, 6·0; Cl, 14·8. $C_{12}H_{14}O_2NCl$ requires N, 5·9; Cl, 14·8%).

Ethyl β-m-*chloroanilinocrotonate* was prepared in the same way with a trace of iodine or *m*-chloroaniline hydrochloride as catalyst; water appeared in about 20 minutes: without a catalyst, there was no appearance of reaction in 1 week. The ester, an almost colourless oil, boiled at 145—148°/1—1·5 mm. with only a trace of decomposition (*s*-di-*m*-chlorophenylurea); yield, 83% (Found: N, 5·9; Cl, 14·6. $C_{12}H_{14}O_2NCl$ requires N, 5·9; Cl, 14·8%). Ethyl β-*p*-chloroanilinocrotonate, described by Jadhav (*loc. cit.*), was prepared by dissolving *p*-chloroaniline in ethyl acetoacetate with gentle warming and when cold adding a trace of catalyst. The turbid mixture crystallised in a vacuum over sulphuric acid; the product, dried on porous tile and recrystallised from alcohol, formed needles, m. p. 55° (Found: N, 5·9. Calc.: N, 5·9%). The times which elapsed before turbidity appeared were: (1) with no catalyst, 20 minutes; (2) hydrochloric acid, 1—2 minutes; (3) iodine, 9 minutes; (4) diethylamine, no action over-night but the mixture crystallised after several days in a vacuum over sulphuric acid.

Ethyl β-*m*-4-xylidinocrotonate was described but not purified or analysed by Conrad and Limpach (*Ber.*, 1888, **21**, 523) and by Späth (*Monatsh.*, 1919, **40**, 93). It was prepared from *m*-4-xylidine as a non-crystallisable oil, b. p. 123—124°/2 mm. (Found: N, 6·1. Calc.: N, 6·0%); yield, almost quantitative. The times which elapsed before water appeared in the reaction mixture were: (1) with no catalyst, over-night; (2) iodine, 5—10 minutes; (3) *m*-4-xylidine hydrochloride, 1—2 hours; (4) diethylamine, over-night.

Ethyl β-p-*xylidinocrotonate* was prepared from *p*-xylidine with a catalyst (no catalyst, over-night; iodine, 42 minutes; *p*-xylidine hydrochloride, about 1 hour; diethylamine, over-night). After drying in a vacuum over sulphuric acid, the non-crystallisable oil had b. p. 132—133°/2—3 mm.; yield, 95%. At higher pressures there was considerable formation of the urea (Found: N, 6·1. $C_{14}H_{19}O_2N$ requires N, 6·0%).

Ethyl β-p-*phenylaminoanilinocrotonate*, CMe(NH·C_6H_4·NHPh):CH·CO_2Et, was prepared by gently warming an equimolecular mixture of ethyl acetoacetate and *p*-aminodiphenylamine

till solution took place and then adding a catalyst after removal from the water-bath (no catalyst, over-night; hydrochloric acid, 3 minutes; iodine, 17 minutes; diethylamine, about 2 hours). The mixture solidified in a vacuum over sulphuric acid; the crystalline product had m. p. 77—78° after recrystallisation from petroleum (b. p. 100—120°); yield, nearly quantitative (Found : N, 9·6. $C_{18}H_{20}O_2N_2$ requires N, 9·5%).

β-p-*Xylidinocrotono*-p-*xylidide*.—Ethyl β-*p*-xylidinocrotonate (5·85 g.) and *p*-xylidine (3·05 g.) were refluxed in petroleum (b. p. above 120°) under a fractionating column for 5 hours; a small quantity of alcohol appeared at the top of the column. The cold solution after filtration from a small quantity of the urea was distilled at 2 mm.; solvent and unaltered reactants passed over. The residue was dissolved in a little petroleum (b. p. 100—120°); the solution on nucleation and standing for several days deposited a small clump of crystals, m. p. 107—108°, identical with β-*p*-xylidinocrotono-*p*-xylidide as shown by comparison with an authentic specimen; yield, 17%.

β-*o*-Chloroanilinocrotono-*o*-chloroanilide was obtained by a similar method on one occasion only in a yield of 3%. The other ethyl β-arylaminocrotonates did not give β-arylaminocrotonoarylamides.

We thank the Governors of this College for a Research Assistantship held by one of us (J. K. T.) and also Imperial Chemical Industries, Ltd., for valuable assistance.

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198. *Crystalline 6-Methyl Glucose. A New Synthesis.*

By D. J. Bell.

6-Methyl glucose was first prepared in an amorphous state by Helferich and Becker (*Annalen*, 1924, **440**, 1) and was later obtained crystalline by Ohle and von Vargha (*Ber.*, 1929, **62**, 2435), who considered it to be the 5-derivative until Levene and Raymond (*J. Biol. Chem.*, 1932, **97**, 751) showed that the methyl group occupied position 6. Helferich and Becker's product has never been crystallised and the initial material (6-*p*-toluenesulphonyl monoacetoneglucose) used in Ohle and von Vargha's procedure is troublesome to prepare.

3 : 5-Benzylidene monoacetone glucose (Brigl and Grüner, *Ber.*, 1932, **65**, 1428; Zervas and Sessler, *Ber.*, 1933, **66**, 1326) ought to yield 6-methylglucose on direct methylation; unfortunately its preparation is relatively wasteful. 6-Acetyl monoacetoneglucose, however, is readily obtainable in one series of operations by acetylation of the crude product of the condensation of acetone and boric acid with glucose, described by von Vargha (*Ber.*, 1933, **66**, 704), no intermediate isolation being necessary. The acetyl compound, shaken with benzaldehyde and phosphoric oxide, gives an 80% yield of the 3 : 5-benzylidene derivative; simultaneous deacetylation and methylation with methyl sulphate and caustic soda then yields crystalline 3 : 5-*benzylidene 6-methyl monoacetoneglucose*. Simultaneous hydrolysis of the benzylidene and *iso*propylidene residues forms crystalline 6-methyl glucose, whose constants compare well with those recorded by the above authors.

Experimental.

6-*Acetyl Monoacetoneglucose*.—Various modifications of the following typical experiment were made without improving the yield. Glucose (75 g.) was treated with acetone, boric acid, and snlphuric acid exactly as described by von Vargha (*loc. cit.*). To the crude product, isolated by removal of the unchanged acetone by distillation, subsequent to neutralisation, 105 g. of acetic anhydride and 75 g. of fused sodium acetate were added and the whole was heated on the water-bath until a brown colour developed (15 mins.). Water (600 ml.) was then added to give a homogeneous solution; after 1 hour this was extracted five times with 100 ml. lots of benzene. The aqueous layer was then extracted ten times with 50 ml. lots of chloroform, the chloroform

freed from acetic acid by shaking with saturated potassium bicarbonate solution, dried over sodium sulphate, and evaporated to dryness in a vacuum, leaving the product as an almost colourless syrup which immediately crystallised on cooling. Recrystallisation from ethyl alcohol gave 27 g. of needles, m. p. 145·5° (corr.), $[\alpha]_D^{18°}$ — 6·7 (in chloroform; l = 4, c = 1·1). Fischer and Noth (*Ber.*, 1918, **51**, 321) reported m. p. 146° and $[\alpha]_D$ — 6·3° (their compound being then considered to be the 3-isomeride).

6-*Acetyl* 3 : 5-*Benzylidene Monoacetoneglucose.*—22 G. of 6-acetyl monoacetoneglucose, 88 ml. of freshly distilled benzaldehyde, and 22 g. of phosphoric oxide were shaken together for 4 hours, 200 ml. of benzene added, and the resulting solution filtered through charcoal. Water (500 ml.) was added to the filtrate, and the whole distilled in a vacuum at 60° until no more benzaldehyde distilled over. The crystalline residue was dissolved in benzene, and the solution washed with water, dried over sodium sulphate, and evaporated to dryness in a vacuum. The residual syrup crystallised immediately and on recrystallisation from alcohol gave needles, m. p. 126—127°. Yield, 25 g. (84·7%). Brigl and Grüner (*loc. cit.*) report m. p. 126—127°.

3 : 5-*Benzylidene* 6-*Methyl Monoacetoneglucose.*—50 G. of the above compound, dissolved in 250 ml. of acetone, were methylated at 50° with 65 g. of methyl sulphate (4 mols.) and 160 ml. of 30% caustic soda solution. The reagents were added in 1/10-portions at 10 minute intervals. On evaporation of the acetone, a crystalline mixture of methylated and unmethylated deacetylated material separated. After two further treatments in acetone the product was dissolved in benzene and washed with water, and the solution dried over sodium sulphate and evaporated in a vacuum. The 40 g. of crystalline material obtained, on recrystallisation from 75% alcohol, left 5 g. of a crystalline residue of unknown composition undissolved. The purified *product* (28 g.) had m. p. 95—96° and $[\alpha]_D^{20°}$ + 3·8° (in chloroform; l = 2, c = 7·0) (Found : OMe, 9·4. $C_{17}H_{22}O_6$ requires OMe, 9·6%).

6-*Methyl Glucose.*—26 G. of benzylidene methyl monoacetoneglucose were heated on the boiling water-bath with 134 ml. of *N*-sulphuric acid and 134 ml. of alcohol until a constant rotation was obtained :

Time (hrs.)	1	1·5	2	2·5	3
$[\alpha]_D$ (calcd. on free sugar)	+41·0°	49·0°	49·7°	53·5°	54·3° (const.)

The alcohol was distilled off, the acid neutralised by barium carbonate, and the filtered solution evaporated in a vacuum. The residual colourless syrup crystallised immediately; it was dissolved in alcohol and filtered through charcoal, an equal volume of benzene added, and the solution evaporated to half bulk. On cooling, large needles separated, m. p. 143—145° (heating at the ordinary rate). Ohle and von Vargha reported 143—144° as the m. p. of their supposed 5-methyl derivative, and Levene and Raymond 153—154° on rapid heating. Recrystallisation of our product and various rates of heating failed to raise the m. p. above 145° (Found : OMe, 16·0. Calc. for $C_7H_{14}O_6$: OMe, 15·99%).

Dissolved in water, the crystals showed downward mutarotation, the points when plotted graphically giving a perfectly smooth curve (c = 3, l = 2) :

Time (mins.)	0	5	10	30	60	120	20 (hrs.)
$[\alpha]_D^{16°}$	+ 110° (by extrapolation)	102·5°	98·7°	89·9°	81·1°	73·7°	55·0° (const.)

Ohle and von Vargha reported, for supposedly 5-methyl glucose, $[\alpha]_D$ 101·2° (3 mins.), falling to 59·92° (const.) in 3 hours. Levene and Raymond, for two samples of 6-methyl glucose, reported 101·8° (1 min.), falling to 56·0° (const.; 5 hrs.), and 104·5°, falling to 58·5°.

6-*Methyl Glucosazone.*—In order to confirm the constitution of the sugar described above, the osazone was prepared and recrystallised from methyl alcohol until a constant sharp m. p. was obtained, 190° (corr.) (Found : OMe, 8·3. Calc. for $C_{19}H_{22}O_4N_4$: OMe, 8·3%). The product consisted of large, pale yellow needles, which, when dissolved in ethyl alcohol, showed mutarotation (l = 2, c = 0·47) :

Time (hrs.)	0	2	16	36	60 and 72
$[\alpha]_D$	−75°	−64·2°	−53·6°	−52·5°	−48°

The following constants are recorded for 6-methyl glucosazone in the literature :

Authors.	M. p.	$[\alpha]_D$ in alcohol. Initial.	Final.
Ohle and von Vargha (1)	178°	−69·6°	−46·4°
Helferich and Günther (2)	184—187 (corr.)	−69, no mutarotation	
Levene and Raymond (3)	183	−70·5	−44·0

(1) *Ber.*, 1929, **62**, 2425. (2) *Ber.*, 1931, **64**, 1276. (3) *J. Biol. Chem.*, 1932, **97**, 751.

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PHYSIOLOGICAL LABORATORY, ABERDEEN. [*Received, April 7th*, 1936.]

199. *Chromic Picrate.*

By HERBERT J. S. KING.

NORMAL chromic picrate has not previously been isolated. Silberrad and Phillips (J., 1908, **93**, 486) attempted to prepare it by concentrating the filtrate from equivalent quantities of barium picrate and chromic sulphate, but the product was a basic picrate of approximate composition $Cr(C_6H_2O_7N_3)_3,2CrO(C_6H_2O_7N_3)$.

The normal picrate has now been prepared by treating a solution of violet hexa-aquochromic chloride, $[Cr(H_2O)_6]Cl_3$, with 3 mols. of silver picrate. From the filtrate, by concentration at room temperature, yellowish-green needles of the *octahydrate* were obtained; these yielded on dehydration dark brown anhydrous *chromic picrate*, which sintered with decomposition at 94° and exploded feebly at 240°. The readiness with which dehydration occurs differentiates hydrated chromic picrate from hexa-aquochromic chloride, which can be kept indefinitely over sulphuric acid without loss in weight.

The picrate radical in an aqueous solution of the hydrated picrate was immediately and completely precipitated in the cold by hexa-amminochromic nitrate. However, the values obtained for the molecular conductivity of the octahydrate at 0° were 20% lower than those expected for hexa-aquochromic picrate, based on the values recorded by Bjerrum (*Z. physikal. Chem.*, 1907, **59**, 336) for the molecular conductivity of hexa-aquochromic chloride, and by Ferguson and Vogel (*Phil. Mag.*, 1927, **4**, 239) for the mobility of the picrate ion. These observations suggest that the aqueous solution of the octahydrate contains an equilibrium mixture of $[Cr(H_2O)_6](C_6H_2O_7N_3)_3$ with $[Cr(H_2O)_5(C_6H_2O_7N_3)](C_6H_2O_7N_3)_2$ or $[Cr(H_2O)_4(C_6H_2O_7N_3)_2](C_6H_2O_7N_3)$.

An attempt to prepare dichlorotetra-aquochromic picrate from dichlorotetra-aquochromic chloride and 1 mol. of silver picrate yielded green needles which, however, contained no chlorine and proved to be essentially chromic picrate.

When hexa-aquochromic chloride was treated with 3 mols. of silver nitrite, the resulting violet solution of hexa-aquochromic nitrite evolved oxides of nitrogen when left in a vacuum over sulphuric acid, and chromic nitrite could not be isolated from it.

EXPERIMENTAL.

Hexa-aquochromic chloride was prepared by Higley's method (*J. Amer. Chem. Soc.*, 1904, **26**, 620). Silver picrate was obtained by boiling excess silver oxide with picric acid; it was an orange monohydrate, not the yellow anhydrous salt as stated by Silberrad and Phillips (*loc. cit.*) (Found: H_2O, 5·1. Calc. for $C_6H_2O_7N_3Ag,H_2O$: H_2O, 5·1%). The monohydrate was stable if air-dried, and yielded the yellow anhydrous salt when heated at 85° for 20 minutes.

Chromic Picrate.—Octahydrate. Hexa-aquochromic chloride (5 g.) was mixed with 18·9 g. of silver picrate and 25 c.c. of water in an ice-cooled mortar, and left for ½ hour, with occasional trituration. After being filtered from silver chloride, the dark brown solution was concentrated at room temperature over sulphuric acid in a vacuum. When practically all the water had been removed, long yellowish-green needles separated, and were recrystallised from water at 25°, 10 g. dissolving in 4 c.c. On cooling in ice, the yellowish-green needles were again obtained, and were dried on plate over soda-lime in a vacuum [Found: Cr, 6·0; N, 14·2; H_2O, 16·4. $Cr(C_6H_2O_7N_3)_3,8H_2O$ requires Cr, 5·9; N, 14·3; H_2O, 16·4%].

The conductivity data at 0° were as follows :

v	64	128	256	512	1024	2048
λ_0.	89·4	103·9	117·1	130·6	143·7	159·2

When the solution of chromic picrate was concentrated by boiling, it yielded green needles of a basic picrate, sparingly soluble in cold water. *Anhydrous salt.* At 85° the octahydrate lost 5 mols. of water in 15 minutes, and was completely dehydrated in 24 hours. Dehydration for a month over sulphuric acid also afforded the *anhydrous* salt [Found: Cr, 7·0; N, 17·0. $Cr(C_6H_2O_7N_3)_3$ requires Cr, 7·1; N, 17·1%]. Its ignition point (*i.e.*, the lowest temperature at which immediate ignition occurred on dropping a small portion into a tube heated in a metal-bath) was 240°. It dissolved readily and completely in cold dry acetone and pyridine to deep brown solutions, was sparingly soluble in alcohol, and insoluble in benzene and in ether. It was decomposed by cold water into picric acid and green basic chromic picrate.

When anhydrous chromic picrate was treated with liquid ammonia, and the excess ammonia allowed to evaporate, a mixture of chromammine picrates was obtained, in which 3·5 mols. of ammonia were associated with each atom of chromium.

Action of Hexa-amminochromic Nitrate (1½ *Mols.*) *on Hydrated Chromic Picrate.*—On mixing the cold aqueous solutions, bright yellow needles were immediately precipitated. No further precipitate was produced on adding more of the nitrate to the filtrate and leaving it over-night {Found: Cr, 7·6; NH_3, 15·0; N, 26·8. $[Cr(NH_3)_6](NO_3)(C_6H_2O_7N_3)_2$ requires Cr, 7·7; NH_3, 15·2; N, 27·1%}. Hexa-amminochromic tripicrate is precipitated only in presence of excess of picrate (see King, J., 1924, **125**, 1333).

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200. *The Dipole Moments of Certain Polynitro-compounds.*

By H. O. Jenkins.

Dielectric-constant and density measurements have been made for dilute solutions of (*a*) benzene in chloroform, (*b*) *p*-dinitrobenzene in chloroform, (*c*) 1 : 3 : 5-trinitrobenzene in chloroform, (*d*) trinitromesitylene in benzene, (*e*) 1 : 3 : 5-trinitro-2 : 4 : 6-triethylbenzene in benzene and in carbon tetrachloride. Some of the results were briefly described in a preliminary note (Jenkins, *Nature*, 1934, **134**, 217). In the meantime a paper on this subject has been published by Le Fèvre and Le Fèvre (J., 1935, 957), but their conclusions cannot be accepted.

Several polynitro-compounds have been investigated, with surprising results. Lütgert (*Z. physikal. Chem.*, 1931, *B*, **14**, 450) measured the polarisations of several hexasubstituted benzene derivatives in benzene, and, finding considerable differences between $_{\infty}P_2$ and $_{E}P_2$, ascribed the residue entirely to atomic polarisation. The compound 1 : 3 : 5-tribromo-2 : 4 : 6-trinitrobenzene was said to have an atomic polarisation of 28 c.c., and trinitromesitylene 20 c.c. *p*-Dinitrobenzene and 1 : 3 : 5-trinitrobenzene have also been studied in benzene and naphthalene with similar results, and atomic polarisations or electric moments ascribed depending on the investigator. It is clear that any interpretation given will depend on what structure is assigned to the nitro-group. Since benzene or naphthalene had been consistently used as solvents, there was the possibility that the results were spurious owing to the existence of complexes in solution. The insolubility of *p*-dinitrobenzene and 1 : 3 : 5-trinitrobenzene in other non-polar solvents made the choice of a polar solvent inevitable for them. Polarisations of benzene in chloroform were measured to check the reliability of the solvent.

Experimental.

Materials.—*Chloroform.* Hopkin and Williams's material was shaken with concentrated sulphuric acid, then with potassium hydroxide solution, washed with water, and fractionally distilled over phosphoric oxide before use. The density of material prepared on different occasions varied slightly.

1 : 3 : 5-*Trinitrobenzene.* 40 G. of *m*-dinitrobenzene, 130 g. of fuming nitric acid, and 250 g. of fuming sulphuric acid were heated together for one week at 140—150°. The mixture was

allowed to cool, poured into water, and the solid filtered off, washed, and recrystallised three times from aqueous acetic acid; m. p. 122°.

1 : 3 : 5-*Trinitro*-2 : 4 : 6-*triethylbenzene*. The method of Gattermann, Fritz, and Beck (*Ber.*, 1899, **32**, 1122) was used to prepared triethylbenzene, and this was nitrated and recrystallised from glacial acetic acid; m. p. 110°.

The other compounds were prepared or purified in the usual ways.

Measurements.—The dielectric constants and densities were measured at 25° as described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668). Single-solution condensers were used, and the cell described by Jenkins and Sutton (J., 1935, 609) was used for chloroform solutions. The data are collected in the following tables; ϵ_{25° is the dielectric constant, $d_{4^\circ}^{25^\circ}$ the density, f_2 the mol.-fraction of solute, ${}_{\infty}P_2$ the total polarisation of solute at infinite dilution, ${}_{E}P_2$ the calculated electron polarisation for $\lambda = 5890$ A., and ${}_{\lambda=\infty}P_2$ is the electron polarisation at infinite wave-length. The usual atomic and group refractions have been used to calculate ${}_{E}P_2$.

Benzene in chloroform.

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	4·726	1·4806	—
0·02341	4·627	1·4646	26·8
0·04451	4·549	1·4502	27·9
0·07104	4·448	1·4323	27·9

${}_{\infty}P_2 = 27{\cdot}5 \pm 0{\cdot}5$, ${}_{E}P_2$ (calc.) $= 26{\cdot}2$.

1 : 3 : 5-*Trinitrobenzene in chloroform.*

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	4·725	1·4800	—
0·00604	4·694	1·4822	41·2
0·00903	4·679	1·4833	41·4

${}_{\infty}P_2 = 41{\cdot}3 \pm 0{\cdot}5$, ${}_{E}P_2$ (calc.) $= 44{\cdot}7$, ${}_{E}P_2$ (meas.) $= 43{\cdot}5 \pm 0{\cdot}4$, ${}_{\lambda=\infty}P_2 = 41{\cdot}7 \pm 0{\cdot}4$.

1 : 3 : 5-*Trinitro*-2 : 4 : 6-*triethylbenzene in benzene.*

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	2·2727	0·8738	—
0·00641	2·2779	0·8800	84·6
0·00880	2·2809	0·8824	86·0

${}_{\infty}P_2 = 85{\cdot}0 \pm 1{\cdot}0$, ${}_{E}P_2$ (calc.) $= 72{\cdot}6$.

p-*Dinitrobenzene in chloroform.*

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	4·725	1·4797	—
0·00908	4·677	1·4799	33·8
0·00995	4·674	1·4800	34·4
0·01141	4·666	1·4800	34·2

${}_{\infty}P_2 = 34{\cdot}1 \pm 0{\cdot}5$, ${}_{E}P_2$ (calc.) $= 38{\cdot}5$.

Trinitromesitylene in benzene.

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	2·2727	0·8738	—
0·00485	2·2770	0·8782	72·5
0·00599	2·2784	0·8796	73·1
0·00675	2·2780	0·8803	71·0

${}_{\infty}P_2 = 72{\cdot}2 \pm 0{\cdot}5$, ${}_{E}P_2$ (calc.) $= 59{\cdot}2$.

1 : 3 : 5-*Trinitro*-2 : 4 : 6-*triethylbenzene in carbon tetrachloride.*

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	P_2.
0·00000	2·2298	1·5848	—
0·00505	2·2340	1·5811	84·2
0·00642	2·2366	1·5801	84·9
0·00766	2·2375	1·5792	84·0
0·00819	2·2380	1·5788	84·0
0·01100	2·2410	1·5768	83·6

${}_{\infty}P_2 = 84{\cdot}1 \pm 0{\cdot}5$, ${}_{E}P_2$ (calc.) $= 72{\cdot}6$.

DISCUSSION.

Benzene in chloroform gives a total polarisation of $27{\cdot}5 \pm 0{\cdot}5$, in satisfactory agreement with 27·0 found by Smyth (*J. Amer. Chem. Soc.*, 1933, **55**, 453) by the gas temperature method. For 1 : 3 : 5-trinitrobenzene ${}_{\infty}P_2$ is found to be $41{\cdot}3 \pm 0{\cdot}5$; Le Fèvre and Le Fèvre (*loc. cit.*) found 46·6. The electronic polarisation at $\lambda = 5890$ A. is calculated to be 44·7. Le Fèvre and Le Fèvre took the difference ${}_{\infty}P_2 - {}_{E}P_2 = 1{\cdot}9$ c.c., and translated this with the aid of an empirical rule into a gas electric moment of 0·4 *D*. The finite moment found is used in their discussion of the structure of the nitro-group. However, an experimental value of ${}_{E}P_2$ is available, *viz.*, $43{\cdot}5 \pm 0{\cdot}4$ (Briegleb and Kambeitz, *Z. physikal. Chem.*, 1934, *B*, **27**, 11). These authors also give the electron polarisation at infinite wave-length as $41{\cdot}7 \pm 0{\cdot}4$. Now the dielectric constant is measured at virtually an infinite wave-length, and strictly speaking, it is the difference (${}_{\infty}P_2 - {}_{\lambda=\infty}P_2$) which should be used to calculate electric moments. The present experimental result shows that this difference is zero, and thus 1 : 3 : 5-trinitrobenzene has no electric moment in the polar solvent chloroform. *p*-Dinitrobenzene is found to have ${}_{\infty}P_2 = 34{\cdot}1 \pm 0{\cdot}5$. Le Fèvre and Le Fèvre found 38·9. From group refractions ${}_{E}P_2$ is calculated as 38·5. These authors again translate their difference of 0·4 c.c. into a gas electric moment of 0·2 *D*. This places too much reliance on their experimental accuracy and on the validity of their conversion rule. Considering that atomic polarisation has been ignored, the correct inference from their results is a zero moment for *p*-dinitrobenzene *in the polar solvent chloroform*. Unless the result presented in this paper is in error, it would seem that ${}_{\lambda=\infty}P_2$ is 3 or 4 c.c. less than ${}_{E}P_2$,

in which case agreement with the measured $_{\infty}P_2$ would be obtained. Unfortunately, there is no value in the literature for the electron polarisation of *p*-dinitrobenzene at infinite wave-length.

Structure of the Nitro-group.—Le Fèvre and Le Fèvre (*loc. cit.*) suggest a pyramidal structure for the $\geqslant$C–NO_2 group, but their arguments are not valid and the structure is untenable. Such a pyramidal structure involves single bonds between the nitrogen and oxygen atoms. Now the single bond distance has been shown to be 1·37 ± 0·02 A., by the diffraction of electrons through α-methylhydroxylamine (Brockway, Beach, and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2693). The double bond distance N=O can be calculated to be 1·22 ± 0·02, by using the usual factor. An experimental value of the nitrogen–oxygen internuclear distance in nitromethane gives 1·21 ± 0·02 A. (Brockway, Beach, and Pauling, *loc. cit.*). Pauling and others have also shown that, although a bond may have any intermediate character between the extremes of a pure single and a pure double bond, yet a small amount of double-bond character causes a large decrease in interatomic distance. The nitrogen–oxygen distance in the nitro-group is essentially a double-bond distance, and the structure is a resonating one. This demands a coplanar arrangement.

The argument for the pyramidal structure is commenced by the statement that the force constant characterising the links in an aryl nitro-group is greater than that for a single and less than that for a double bond. There is some discrepancy here. Bond force constants are related to internuclear distances. Badger (*J. Chem. Physics,* 1934, **2**, 28) gives the relation $k_0(r_e - d)^3 = 1{\cdot}86 \times 10^5$ for diatomic molecules, where r_e is the equilibrium internuclear distance and d is a constant depending only on the rows in the periodic table in which the two elements are located. It seems that the single-bond force constant has been calculated from nitrogen dioxide data, but this has a resonating structure and should give a double-bond force constant. Also the double-bond force constant has been calculated from data on nitrous oxide, which was given the old symmetrical structure. Pauling (*Proc. Nat. Acad. Sci.*, 1932, **18**, 293) has shown that the wave function for the nitrous oxide molecule is approximately represented by the sum of the wave functions for unsymmetrical structures with equal coefficients. Finally, it should be mentioned that the suggested finite moment for dinitrogen tetroxide (Zahn, *Physikal. Z.*, 1933, **34**, 461) is quite incompatible with the conclusions of Harris and King (*J. Chem. Physics,* 1934, **2**, 51) from infra-red absorption spectra. These authors require two configurations of nearly the same energy in which the nitro-groups lie in the same plane or are mutually perpendicular. Both configurations have zero electric moment, and the gas temperature experiments of Williams Schwingel, and Winning (*J. Amer. Chem. Soc.*, 1934, **56**, 1427) show that this is so.

The Increase of Electric Moment.—Most molecules have a dipole moment in solution less than in the gaseous state. A number of compounds are now known, however, which show an enhanced moment over that required by the structure. This paper is not concerned with molecules such as hydrogen chloride, but with molecules which are probably non-polar, showing, however, an electric moment in non-polar solvents. Table I gives the relevant data. The electric moments therein (μ, in Debye units) have been obtained from the General Discussion on Dipole Moments (Faraday Society, 1934), with the exception of the results presented now, and those for quinone (Le Fèvre and Le Fèvre, J., 1935, 1697; Hammick, Hampson, and Jenkins, *Nature*, 1935, **136**, 990), for tetramethyl*cyclo*butane-1 : 3-dione (*idem, ibid.*), and for the mercuric halides (Curran and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 2162).

Some investigators have considered that the solution method gives the dipole moment of the free molecule and have thus been led to erroneous conclusions. For example, Curran and Wenzke (*loc. cit.*) stated that the configurations of the mercuric halides are non-linear, since the electric moments in dioxan are considerable. This non-linearity is disproved by the crystal structure evidence and by the gas-temperature dielectric-constant experiments of Braune and Linke (*Z. physikal. Chem.*, 1935, *B*, **31**, 12). It is suggested that Le Fèvre and Le Fèvre have been similarly misled in the case of the symmetrical polynitrobenzenes, for Hertel and Romer (*ibid.*, 1933, *B*, **22**, 267), from a study of the crystal structure of picryl iodide and bromide, consider that symmetry considerations require planar molecules.

TABLE I.

Molecule.	Solvent.	μ.
p-Di-iodobenzene	Benzene	0·2
p-Dibromobenzene	,,	0·2
p-Dichlorobenzene	,,	0·2
p-Benzoquinone	,,	0·7
Tetramethyl*cyclo*butane-1 : 3-dione	,,	0·73
p-Cyanonitrobenzene	,,	0·7
p-Dinitrobenzene	,,	0·6
1 : 3 : 5-Trinitrobenzene	,,	0·8
Trinitromesitylene	,,	0·8
1 : 3 : 5-Trinitro-2 : 4 : 6-triethylbenzene	,,	0·8
1 : 3 : 5-Tribromo-2 : 4 : 6-trinitrobenzene	,,	1·1
Diphenylmercury	Decalin	0·54
Di-*p*-tolylmercury	,,	0·74
Di-*p*-fluorophenylmercury	,,	0·87
Di-*p*-bromophenylmercury	,,	0·92
Di-*p*-chlorophenylmercury	,,	1·11
Mercuric chloride	Dioxan	1·29
Mercuric bromide	,,	1·06
Mercuric iodide	,,	0·58

These polar "non-polar" compounds have a further peculiarity in that their total polarisations, although exceeding the electron polarisation, are independent of temperature.

It will now be shown that the existence of the dipole moment and the invariance of the polarisation with temperature can be given a general explanation provided that certain simple assumptions are made. These are :

(*a*) That there is only one molecular species in the gas.

(*b*) That in solution, on account of solute–solvent forces, the moment of a particular link in different molecules has no constant value but fluctuates about a most probable value. A Gaussian distribution law of the following form will be assumed :

$$P(\mu) = Ce^{-\alpha(\mu/\mu_0 - 1)^2/T}$$

with the normalisation condition

$$\int_{-\infty}^{+\infty} P(\mu) \, . \, d\mu = 1$$

Here, μ_0 is the most probable value of μ, T is the absolute temperature, and α and C are constants; α is probably a constant only for a group of similar compounds, *e.g.*, for *p*-derivatives of benzene. This distribution formula assumes greater fluctuations the higher the temperature and the greater the value of μ_0.

(*c*) That changes in the moment of any one molecule are slow relative to its time of relaxation in the medium in question.

(*d*) That each group moment is assumed to be independent.

First, consider the case of a monosubstituted benzene derivative, say nitrobenzene. Its effective moment $({}_1\overline{\mu^2})^{1/2}$ can be obtained from the equation

$${}_1\overline{\mu^2} = \frac{\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu}{\mu_0} - 1\right)^2} \mu^2 \, . \, d\mu}{\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu}{\mu_0} - 1\right)^2} d\mu}$$

i.e.,

$${}_1\overline{\mu^2} = \mu_0^2(1 + T/2\alpha) \qquad (1)$$

Now consider the case of a symmetrical disubstituted benzene derivative, say *p*-dinitrobenzene. It may be seen qualitatively that, owing to the independence of the fluctuations in the individual group moments, at any instant some molecules are non-polar, but that in most molecules the groups have different moments and there is therefore a resultant moment. By assumption (*c*), this causes an extra polarisation. Denoting the two group moments by μ_1 and μ_2, we get the square of the effective moment given by

$${}_2\overline{\mu^2} = \frac{\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_1}{\mu_0} - 1\right)^2} d\mu_1 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_2}{\mu_0} - 1\right)^2} (\mu_2 - \mu_1)^2 \, . \, d\mu_2}{\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_1}{\mu_0} - 1\right)^2} d\mu_1 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_2}{\mu_0} - 1\right)^2} d\mu_2}$$

On evaluation, this reduces to

$$_{2}\overline{\mu^2} = \mu_0^2 T/\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Similarly, in the case of a symmetrical trisubstituted benzene derivative, say 1 : 3 : 5-trinitrobenzene, we have

$$_{3}\overline{\mu^2} = \frac{\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_1}{\mu_0}-1\right)^2} d\mu_1 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_2}{\mu_0}-1\right)^2} d\mu_2 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_3}{\mu_0}-1\right)^2} (\mu_1^2 + \mu_2^2 + \mu_3^2 - \mu_1\mu_2 - \mu_1\mu_3 - \mu_2\mu_3) d\mu_3}{\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_1}{\mu_0}-1\right)^2} d\mu_1 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_2}{\mu_0}-1\right)^2} d\mu_2 \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{T}\left(\frac{\mu_3}{\mu_0}-1\right)^2} d\mu_3}$$

which gives on evaluation

$$_{3}\overline{\mu^2} = 3\mu_0^2 T/2\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since α is essentially positive and finite, equations (2) and (3) predict finite electric dipole moments for *p*-dinitrobenzene, 1 : 3 : 5-trinitrobenzene, and similar compounds. Also, the effective moment in, say, a disubstituted benzene derivative is directly proportional to μ_0, the most probable value of the moment of the monosubstituted derivative. This is supported by experiment. *p*-Dinitrobenzene has an electric moment of 0·6 in benzene, and *p*-dichlorobenzene has the value 0·2—0·3. The results given for the mercury compounds in Table I also support this conclusion.

Furthermore, although 1 : 3 : 5-trinitrobenzene, 1 : 3 : 5-trinitro-2 : 4 : 6-triethylbenzene, and trinitromesitylene all show the same moment in benzene and in carbon tetrachloride, because the C–alkyl link moment is small and would be expected to produce little effect, yet 1 : 3 : 5-tribromo-2 : 4 : 6-trinitrobenzene has a moment of 1·1, because the C–Br link moment is considerable. It is interesting to notice that, according to Höjendahl (*Physikal. Z.*, 1928, **30**, 391), 1 : 5-dinitronaphthalene has an electric moment of 0·6 in benzene, a value close to that for *p*-dinitrobenzene. The temperature variation will now be considered. Since the orientation polarisation is given by $P_O = K\overline{\mu}^2/T$ and by equation (2), for example, $\overline{\mu}^2 = \mu_0^2 T/\alpha$, we get $P_O = K\mu_0^2/\alpha$, an expression invariant with respect to temperature. This again is supported by experiment. Le Fèvre and Le Fèvre (*loc. cit.*) find P_O for *p*-dinitrobenzene and 1 : 3 : 5-trinitrobenzene to be independent of temperature in the range measured, and similar results have been obtained for *p*-benzoquinone (*idem*, J., 1935, 1696).

If an electric moment of 0·6 is assumed for *p*-dinitrobenzene, equations (2) and (3) enable the moment of 1 : 3 : 5-trinitrobenzene to be calculated. The value obtained, 0·74, is in good agreement with that found, 0·8. It may be mentioned that this method of calculating electric moments gets into no difficulty when meta-compounds are considered, and also does not remove the well-known "ortho" anomaly. In addition to other factors entering, our assumption of link independency is probably not true in this case.

It would be difficult rigorously to derive the distribution formula used, and at present it may be regarded as empirical. However, it is reasonable that the formula should give greater fluctuations the higher the temperature and the greater the value of μ_0.

A few consequences of the proposed explanation of electric moments developed by non-polar substances in solution may be mentioned. First, care must be taken in the interpretation of such results as the finite moment of 0·5 found by Weissberger (*Trans. Faraday Soc.*, 1934, **30**, 884) for 1 : 4-dichloronaphthalene. This is regarded as being due to a shift of electrons in the molecule towards the substituents. There may be real evidence for this shift from other sources, but the dipole-moment evidence does not conclusively prove it. Secondly, since all non-polar substances will show the effect in some degree, atomic polarisations determined from the dilute solution method will be on the high side.

Summary.

An explanation is proposed for the electric moments of symmetrical molecules in solution, based on an assumed fluctuation of link moments about a most probable value. The theory explains the temperature invariance of the orientation polarisation, and relates the

electric moment developed in solution by such compounds as 1:4-dinitrobenzene to the most probable value of the moment of mononitrobenzene in the same solvent. Some consequences of the theory are discussed and it is considered that atomic polarisations determined by the dilute solution method are on the high side.

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201. *Acid Salts of Monobasic Organic Acids. Part II.*

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IT has been shown (J., 1933, 1016) that extensive compound formation between racemic mandelic acid and its normal potassium, sodium, lithium, barium, strontium, and calcium salts takes place, and that acid salts of these metals can be isolated. These series have now been completed by a study of the solubility curves for the rubidium, cæsium, ammonium, and magnesium salts at 25°. The system containing thallous mandelate has also been included.

Data relating to the number and stability of the acid salts formed are tabulated below. There is no obvious correlation between the extent of compound formation and electrochemical character of the metal, or between the solubility of the normal salt and the number of acid salts formed, for the systems containing rubidium, cæsium, and ammonium mandelates, all of which are more soluble than potassium mandelate, give fewer acid salts.

Metal.	Acid salts isolated.*	Stability in water.	Metal.	Acid salts isolated.	Stability in water.
Cs	1 : 1	Stable	Li	1 : 1	Stable
Rb	3 : 1	Stable	NH_4	3 : 1	Unstable
	1 : 1	Unstable		1 : 1	Stable
K	3 : 1	Stable	Tl	1 : 1	Stable
	2 : 1	Unstable	Ba	1 : 1	Stable
	1 : 1	Unstable	Sr	1 : 1	Stable
Na	3 : 1	Stable	Ca	1 : 1	Stable
	1 : 1	Stable	Mg	1 : 2	Unstable †

* The ratio is that of mols. of free acid to mols. of normal salt. † Crystallises as a dihydrate.

It has been frequently pointed out, however, that compounds may be present in solution which cannot be isolated in the solid state owing to their solubility conditions being unsuitable.

The effect of addition of metallic mandelates on the solubility of the acid has been studied as in Part I by plotting the concentration of acid against that of mandelate. For comparison with the previous results the curves for sodium and potassium have been included in the diagram (Fig. 1).

Increase in solubility of mandelic acid in presence of normal mandelates.

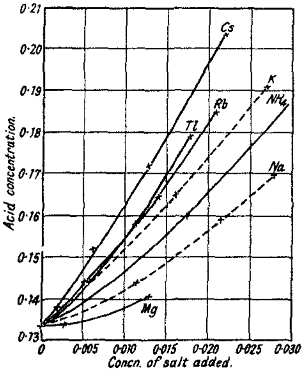
(All results are given in g.-equivs. per 100 g. of H_2O.)

Solubility of mandelic acid in water at 25° = 0·134.

Acid.	Salt.	Acid.	Salt.	Acid.	Salt.	Acid.	Salt.
Cæsium.				*Rubidium.*			
0·138	0·002	0·172	0·013	0·144	0·005	0·185	0·021
0·151	0·006	0·204	0·022	0·165	0·014		
Thallous.				*Ammonium.*			
0·135	0·0014	0·179	0·018	0·160	0·017	0·205	0·037
0·144	0·006	0·209	0·024				
0·158	0·011			*Magnesium.*			
				0·134	0·003	0·141	0·013
Sodium.				*Potassium.*			
0·144	0·0114	0·170	0·028	0·144	0·005	0·191	0·027
0·159	0·021			0·165	0·016		

The order of the metallic mandelates with regard to their effect on the solubility of the acid is as follows : Cs, Tl, Rb, K, NH_4, Na, Mg. We might conclude from these results that the tendency towards complex formation is in the same order, greatest for cæsium and least for magnesium. We have, however, decided that other factors, principally that of the effect of variation in ionic size, which leads to a varying salting-out effect, should be considered in more detail. The two factors, *viz.*, compound formation and salting out, will affect the solubility of the acid in opposite directions. A study of the curves showing the salting-out action of a series of metallic salts with a common ion (chlorides, nitrates, etc.) upon other weak electrolytes, proves that the order and the extent of the effect produced by the metallic ion is similar to the effect found in the present investigation. We hope, by studying the variation in solubility of mandelic acid in presence of a series of chlorides of the alkalis and alkaline earths, to eliminate as far as possible the salting-out effect found in the case of the metal mandelates, and so to obtain a more exact criterion of the extent of compound formation in such solutions.

Fig. 1.



Experimental.

Rubidium Mandelate.—60 G. of rubidium sulphate dissolved in water were treated with a slight excess of concentrated barium hydroxide solution. Barium sulphate was filtered off, and excess barium precipitated by passage of carbon dioxide through the solution. The filtrate was evaporated on the water-bath to small bulk, and neutralised with mandelic acid. The gum obtained on evaporation was thoroughly dried at 90° in a vacuum. The resulting glass was dissolved in as small an amount of methyl alcohol as possible, and the mandelate precipitated as a fine powder by addition of 500 c.c. of acetone. This procedure was repeated to give a pure product (Found : Rb, 36·3. Calc. : Rb, 36·1%).

Cæsium Mandelate.—The normal salt, obtained in the usual way from mandelic acid (50 g.) and cæsium carbonate (50 g.), was crystallised from methyl alcohol, forming fine needles (Found : Cs, 46·9. Calc. : Cs, 46·8%).

Acid Cæsium Mandelate.—Only one acid salt could be isolated in preliminary experiments. 30 G. of mandelic acid and 9·6 g. of cæsium carbonate were dissolved in water and the solution evaporated to small bulk. On further concentration in a desiccator, the salt separated in short pointed prisms; after being washed and dried, it contained 34·7% of acid ($C_8H_8O_3,C_8H_7O_3Cs$ requires 34·9%). An attempt to prepare the 3 : 1 acid salt was unsuccessful, the solid obtained being almost pure acid.

Ammonium Mandelate.—20 G. of mandelic acid dissolved in 150 c.c. of water were neutralised with ammonia, the solution was evaporated to a gum, and 100 c.c. of acetone added. The salt which separated was crystallised from aqueous acetone (10% water) and dried at room temperature. Prolonged evacuation was necessary to remove the last traces of acetone, but on heating, the salt decomposed with evolution of ammonia. The mandelate was also prepared by passing dry ammonia into an ethereal solution of mandelic acid (McMaster, *J. Amer. Chem. Soc.*, 1915, **36**, 1916), the precipitated salt being collected and dried as before.

Thallous Mandelate.—This salt was prepared from thallous sulphate as for the rubidium salt; it crystallised well from aqueous methyl alcohol (1 : 1) (Found : Tl, 57·5. Calc. : Tl, 57·5%).

Magnesium Mandelate.—20 G. of mandelic acid were neutralised with 2·7 g. of magnesium oxide, the solution boiled for some time, and filtered. After standing for several days at room temperature, the salt slowly crystallised out. In view of the discordant values published for

the solubility of magnesium mandelate (see p. 871), the salt was also prepared by a different method. Concentrated solutions containing equivalent amounts of magnesium chloride and potassium mandelate were mixed and kept for some time; the precipitated salt was washed thoroughly and dried at 25° [Found: Mg, 7·3; H_2O, 3·1. Calc. for $(C_8H_7O_3)_2Mg,\frac{1}{2}H_2O$: Mg, 7·4; H_2O, 2·7%].

The solubility determinations were carried out as described previously.

1. *The System Mandelic Acid–Rubidium Mandelate–Water.*—In the earlier experiments with dilute solutions of rubidium mandelate, filtration was carried out in the thermostat as described previously. The more viscous solutions encountered at higher concentrations had to be filtered outside the thermostat, with use of suction; a Jena sintered-glass funnel was used, and before filtration, both funnel and receiving vessel were warmed to about 25°. Filtration by this means was complete in such a short time that there could be little change in the equilibrium of the systems.

The residue method of Schreinemakers was used in the analysis of the solid phase, since with the very viscous solutions obtained the mother-liquor could not be satisfactorily removed from the solid by simply pressing on a porous plate.

Rubidium was determined by evaporation to dryness and conversion into sulphate.

FIG. 2.

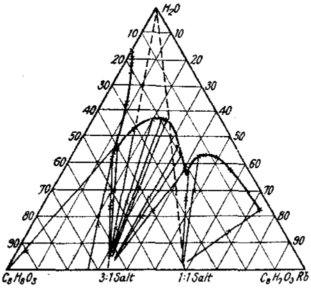
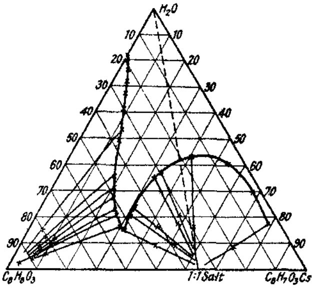


FIG. 3.



The results for this system are collected below, and the corresponding curve given in Fig. 2. Two acid salts are formed, the 3 : 1 salt being stable in contact with its saturated solution, whereas the 1 : 1 salt is not.

Rubidium mandelate.

Composition, %.					Composition, %.				
Solution.		Residue.			Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.	Acid.	Salt.	Acid.	Salt.	Solid phase.
16·95	0·0	—	—	Acid	18·8	24·8	40·3	28·8	3 : 1 Salt
17·8	1·0	—	—	,,	18·3	27·5	—	—	,,
19·5	2·6	—	—	,,	19·7	33·7	38·9	34·1	,,
21·1	3·7	—	—	,,	20·0	36·1	—	—	,,
28·9	7·8	—	—	,,	20·3	38·1	45·0	34·9	,,
40·1	12·9	90·3	2·6	Acid + 3 : 1 salt	21·0	40·1	40·8	37·4	,,
42·2	13·7	61·5	21·8	,,	20·7	41·0	26·8	46·2	1 : 1 Salt
43·5	13·9	53·8	22·4	3 : 1 Salt	14·3	42·1	22·1	46·9	,,
40·5	13·8	52·3	21·8	Acid + 3 : 1 salt	12·5	43·7	—	—	,,
30·8	15·8	55·9	28·5	,,	8·4	48·9	—	—	,,
23·2	20·1	47·0	27·2	3 : 1 Salt	6·5	55·1	—	—	,,
20·1	22·8	44·6	28·5	,,	3·9	73·2	19·0	66·4	,,

2. *The System Mandelic Acid–Cæsium Mandelate–Water.*—The estimation of cæsium as sulphate required several precautions owing to the stability of the hydrogen sulphate and the volatility of cæsium sulphate. After evaporation of the solution, the volatile matter was driven

off at as low a temperature as possible, and a slight excess of sulphuric acid added. The carbc was found to burn off readily at a low red heat under these conditions. A small amount (ammonium carbonate was added to the white residue and the crucible again heated to du redness.

The results are shown below, and in Fig. 3. The 1 : 1 salt alone is formed at 25°, and stable in presence of its saturated solution. This is in agreement with the preliminary exper ments described above.

Cæsium mandelate.

Composition, %.					Composition, %.				
Solution.		Residue.			Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.	Acid.	Salt.	Acid.	Salt.	Solid phase
16·95	0·0	—	—	Acid	50·8	25·6	89·1	6·3	Acid
17·3	0·4	—	—	,,	51·3	27·2	87·9	6·6	,,
18·4	1·4	—	—	,,	52·5	30·7	83·2	10·7	,,
20·1	2·8	—	—	,,	52·5	32·2	45·0	45·3	1 : 1 Salt
22·6	4·5	—	—	,,	47·3	31·9	38·5	52·0	,,
25·6	6·3	—	—	,,	45·6	31·3	—	—	,,
29·1	9·0	—	—	,,	44·3	31·1	40·9	42·3	,,
33·7	12·3	—	—	,,	32·1	32·6	33·4	48·9	,,
36·0	13·5	—	—	,,	29·1	33·4	31·1	47·7	,,
39·4	15·3	79·8	4·9	,,	16·1	40·6	29·0	55·0	,,
45·2	18·3	80·0	7·0	,,	5·3	53·8	—	—	,,
47·4	20·7	84·5	6·8	,,	2·9	67·3	—	—	,,
49·2	22·2	77·7	10·4	,,	3·7	79·2	19·6	72·1	,,
50·0	23·8	94·3	2·8	,,					

3. *The System Mandelic Acid–Ammonium Mandelate–Water.*—The following method (analysis was found to give sufficiently accurate results. The solutions were diluted to a know volume, if necessary, and portions taken. The acid content was determined by titration wit sodium hydroxide solution and methyl-red as indicator. The end-point was detected by com parison of the colour of two solutions, one just acid and the other just alkaline. A measure excess of alkali was then added, and the ammonia boiled off. The excess alkali was titrate with standard hydrochloric acid. This method was applied both to solutions and to mois residues.

The results are collected below, and the curve is shown in Fig. 4. Two acid salts are formec 3 : 1 and 1 : 1, of which only the latter is stable in presence of its saturated solution; the forme is stable over a very short range of concentrations.

Ammonium mandelate.

Composition, %.					Composition, %.				
Solution.		Residue.			Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.	Acid.	Salt.	Acid.	Salt.	Solid phase.
16·95	0·0	—	—	Acid	51·2	25·4	64·0	18·2	Acid
19·1	2·3	—	—	,,	50·9	26·3	76·4	15·1	Acid + 3 : 1 sa
22·7	4·5	—	—	,,	50·5	27·4	62·4	27·5	3 : 1 Salt
24·7	5·6	—	—	,,	49·7	28·7	60·7	28·0	,,
28·0	7·3	—	—	,,	47·0	32·3	60·7	29·6	,,
31·1	8·9	—	—	,,	47·2	32·2	47·5	40·5	1 : 1 Salt
39·7	14·0	—	—	,,	41·1	33·9	42·2	39·4	,,
44·2	15·9	66·4	9·4	,,	35·2	36·1	39·9	42·3	,,
47·1	18·0	—	—	,,	28·3	42·1	35·1	45·2	,,
47·9	19·8	72·0	11·5	,,	25·4	45·7	34·9	47·6	,,
50·8	24·5	—	—	,,	20·7	50·9	—	—	,,
50·4	25·4	—	—	,,	17·2	56·2	30·5	54·1	,,

4. *The System Mandelic Acid–Thallous Mandelate–Water.*—Analyses of the solutions wer carried out by precipitation of thallium as thallous iodide in the cold, and weighing th iodide in a Gooch crucible. At a few points the composition of the solid phase was determine by the residue method, and at others by direct analysis.

The results are given below, with the corresponding curve in Fig. 5. One stable acid sal is formed of the 1 : 1 type.

FIG. 4.

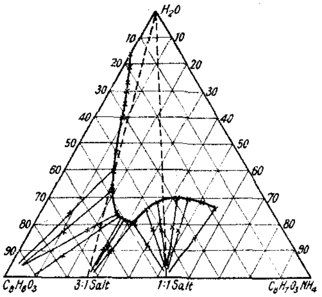
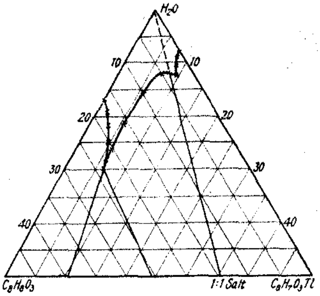


FIG. 5.



Thallous mandelate.

Composition, %.				
Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.
16·95	0·0	—	—	Acid
17·0	0·4	—	—	,,
17·2	0·6	—	—	,,
17·7	1·6	—	—	,,
18·8	3·1	99·5	—	,,
20·4	4·7	—	—	,,
22·6	6·0	50·1	12·4	Acid + 1 : 1 salt
24·0	6·0	28·4	41·4	1 : 1 Salt
20·9	5·8	—	—	,,

Composition, %.				
Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.
16·0	5·4	—	—	1 : 1 Salt
12·2	5·3	30·4	—	,,
9·1	5·7	30·1	—	,,
4·8	7·1	—	—	,,
3·7	8·2	16·5	37·9	,,
2·8	9·5	9·6	—	1 : 1 Salt + normal salt
1·9	8·5	—	—	Normal salt
1·0	8·1	—	—	,,
0·0	7·8	0·0	—	,,

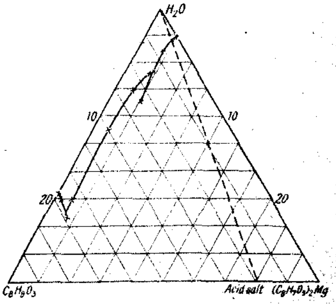
5. *The System Mandelic Acid–Magnesium Mandelate–Water.*—In determinations of this system, 15—20 c.c. of water were used. The amount of magnesium mandelate was determined by ignition to oxide. Owing to the slowness at which the systems attained equilibrium, it was necessary to stir the solutions for much longer than usual (40—60 hours). The solubility of the normal salt was found to be 2·61 g. per 100 g. of solution: McKenzie (J., 1899, **75**, 969) found 1·8 g. at 18°, whereas Findlay and Campbell (J., 1930, 2721) reported 0·95 g. at 25°.

The results for this system are shown below, and the curve is given in Fig. 6. The acid salt was analysed [Found: $Mg(C_8H_7O_3)_2$, 77·6; $C_8H_8O_3$, 17·9; H_2O, 4·2. Calc. for $C_8H_8O_3,2Mg(C_8H_7O_3)_2,2H_2O$: $Mg(C_8H_7O_3)_2$, 77·6; $C_8H_8O_3$, 18·1; H_2O, 4·3%].

Magnesium mandelate.

Acid, %.	Salt, %.	Solid phase.
16·95	0·0	Acid
16·9	0·4	,,
17·3	1·8	,,
16·0	1·4	1 : 2 Salt
9·6	1·4	,,
6·2	1·5	,,
3·7	2·1	,,
3·3	2·3	,,
5·9	2·6	Normal salt
1·7	2·1	,,
0·0	2·6	,,

FIG. 6.



SUMMARY.

The series of solubility curves for the optically inactive systems mandelic acid–metal mandelates–water at 25° has been completed by an examination of the systems for rubidium, cæsium, ammonium, thallous, and magnesium mandelates. The following acid salts have been isolated: $C_8H_8O_3,C_8H_7O_3Rb$; $3C_8H_8O_3,C_8H_7O_3Rb$; $C_8H_8O_3,C_8H_7O_3Cs$; $C_8H_8O_3,C_8H_7O_3NH_4$; $3C_8H_8O_3,C_8H_7O_3NH_4$; $C_8H_8O_3,C_8H_7O_3Tl$; $C_8H_8O_3,2(C_8H_7O_3)_2Mg,2H_2O$.

The effect of variation of the metallic radical upon the extent of compound formation is discussed, and attention directed to one of the factors, namely, ionic size, which tends to obscure the interpretation of the results.

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